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Gas mixing in long pipelines

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Summary—The longitudinal diffusion coefficient in a 3 in. diameter pipe carrying refinery gas over a 9,000 ft distance has been measured by using hydrogen as a tracer. The results show that the formula for the effective diffusion coefficient given by TAYLOR, $K = 7{\cdot}14\, aU\sqrt{c_f}$, may be used for gases as well as for liquids. This means that the Schmidt group has no influence on longitudinal diffusion.

Résumé—En utilisant de l'hydrogène comme indicateur, les auteurs ont mesurés le coefficient de diffusion longitudinal dans une conduite de 3″ (7,62 cm) servant au transport des gaz de raffinerie, sur 9.000 ft (2,743 km). Les résultats prouvent que la formule de TAYLOR pour le coefficient de diffusion effective, $K = 7{,}14\ aU\sqrt{cf}$ est valable pour les gaz comme pour les liquides. En conséquence, le groupe de SCHMIDT est sans influence sur la diffusion longitudinale.

WHEN fluid flows through a pipe with turbulent motion, the dispersion of matter can be predicted from a simple formula given by TAYLOR [5]. He has shown that the longitudinal transfer, relative to a plane moving with the mean velocity of flow in the pipe, follows the ordinary diffusion equation, and the virtual coefficient of diffusion is $K = 7{\cdot}14\, aU\sqrt{c_f}$. a is the radius of the pipe, U the mean flow velocity and c_f the friction coefficient.

The object of the present work was to find out whether this result would be influenced by a wide variation in the Schmidt group $\mu/\rho D$. Such a variation can be achieved by changing from liquids, which were used in all the experiments quoted by TAYLOR, to gases. Experiments on mass transfer from a solid boundary to a turbulent stream have shown [4] that the Schmidt group has an appreciable effect, and a similar result might be expected with longitudinal dispersion in pipes. The experiments described here deal with a 9,000 ft stretch of 3 in. diameter pipeline carrying refinery gas, and the Schmidt group was about 1,000 times smaller than that of previous investigators.

The theory given by TAYLOR refers to a straight pipe, but in the present case the pipe contained a number of sharp bends. Calculations showed that the bends would contribute only 5% of the pressure drop, and it was therefore anticipated that the effect upon the mixing would be small. Part of the interest of the experiments lay in finding out whether this expectation would be justified.

GENERAL PROCEDURE

Following the method of previous workers, a small shot of tracer material was injected at the beginning of the pipeline. The material then moved down the line with the mean velocity, about 8 m.p.h., spreading longitudinally and giving a measurable concentration at the outlet for about 30 seconds. The tracer was hydrogen, and a conductivity meter was used for the analysis. The lag of the instrument was such that it would detect the arrival of the injected slug, but would not give an accurate concentration-time graph. Two shots of hydrogen were therefore injected, with a 4 minute interval. The arrival of the first shot, about 15 minutes after injection,

was detected by the meter connected to the sampling point. 3 minutes 45 seconds later the first of 12 evacuated sample bottles was connected to the line at the sampling point, and by taking the other samples at 3 second intervals, the distribution of hydrogen near the time of arrival of the second shot could be obtained by analysing the samples at leisure.

The pipeline worked at about 200 p.s.i. gauge with a pressure drop of about 8 p.s.i. over the test length, and the latter quantity had to be known accurately for the calculation of c_f. The method used was to connect simultaneously a cylinder to each end of the line, and subsequently to measure the pressure difference between the cylinders on a differential pressure gauge.

EXPERIMENTAL DETAILS

Hydrogen injection

Following the method employed by DANCKWERTS *et al.* [1], a cylinder, fitted with a pressure gauge and connected to the line via a quick acting cock, was filled with hydrogen from a storage cylinder. From the volume of the intermediate vessel (0·170 cu. ft.), the pressure drop on injection (from 400 p.s.i.g. to 260 p.s.i.g.), and the temperature, it was possible to calculate the quantity of hydrogen injected.

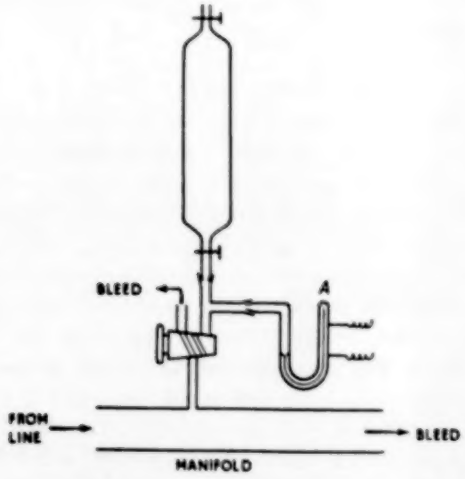

FIG. 1. Sampling arrangement.

Sampling

The sampling arrangement, shown in Fig. 1, was similar to that of DANCKWERTS *et al.* [1]. Evacuated sample bottles of about 100 cc. capacity were connected to the line via a two way cock and a manifold. The sample bottles were at most 6 ft from the pipeline, and by taking a continuous bleed of gas through the manifold and the two way cock at about 20 ft/sec, a lag of only about $\frac{1}{3}$ sec between the line and sample bottle compositions was obtained.

Timing

On turning the two way cock, a thread of mercury rose in the evacuated manometer, and by momentarily joining the platinum wires, made a mark on a uniformly rotating drum. At first it was found that the capillary tube fractured at *A* (Fig. 1), owing to the high velocity of the mercury. This difficulty was overcome by putting a small piece of asbestos wool inside the tube at *A*.

The marks on the drum fixed the time intervals between the samples, and the time of opening the first tap was noted, from a watch, to the nearest second. In this way the sampling was co-ordinated with the injection, which had been made at an agreed time.

Analysis

The Cambridge differential katharometer [2] already employed to detect the arrival of the signal pulse, was adapted to measure the concentration of hydrogen in the sample bottles. When the instrument is operating normally, heat is conducted through the gas from an electrically heated wire to the walls of a small chamber in a metal block. The gas is supplied to the measuring chamber by diffusion through small drillings connected to a hole carrying a continuous flow of gas. The instrument is fitted with two similar chambers for the comparison of gases. The heated wire in each chamber forms an arm of a Wheatstone bridge, and the heating current also serves as a bridge input.

For the analysis of samples, the block was fitted with glass taps so that the measuring chamber could be evacuated, and subsequently connected to the sample bottle. It was found

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that the instrument needed many minutes to give a steady reading after admitting a sample. The time was reduced to about 8 minutes by connecting fresh bottles to both sides of the instrument at once. One bottle contained the sample, and the other contained gas from a cylinder which had been filled from the pipeline just before taking the samples.

The instrument was calibrated by mixing a known volume (about 100 cc) of line gas with a measured volume (about 2 cc) of hydrogen, giving readings of the same order as those in the tests.

A daily gas analysis, using a mass-spectrometer, was done by the refinery, and from these results the density was calculated. On a molecular basis, the gas contained mainly hydrogen, methane, ethane and ethylene, as well as small amounts of propane, propylene and heavier hydrocarbons. There were daily variations in hydrogen content of about 10%. This variation affected the calibration of the katharometer, but did not influence the calculation of the diffusion coefficient K, which depended only on the relative readings of the instrument on any single run.

Measurement of pressure drop

This was done by means of a Budenberg "Microvar" differential pressure gauge reading differences up to 30 lb./sq. in. The cylinders A and E Fig. 2, were filled at opposite ends of the pipeline. With B closed, C and D were connected together, and the pressure difference was read from the gauge G, with a small correction for the volume of pipework between B and C.

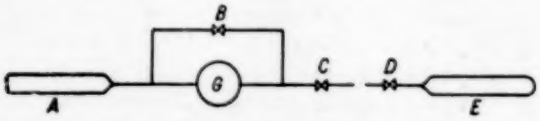

Fig. 2. Pressure drop measurement.

Results

Friction coefficient

Table 1 gives values of the friction coefficient c_f, calculated from the pressure drop and from the simultaneous measurement of the mean velocity by the injection and sampling technique.

Table 1

Density lb./cu. ft.	*Pressure drop* p.s.i.	*Reynolds number* 10^{-5} R	*Friction coefficient* 10^3 c_f
0·73	5·8	2·71	5·2
0·74	5·9	2·76	5·2
0·74	8·6	3·26	5·4

The values are roughly in accordance with the graph given by Goldstein [3] for a roughness to pipe diameter ratio of 0·0015. This graph was used for estimating the friction coefficient at other values of R.

Parameter $K/aU\sqrt{c_f}$

The katharometer readings, giving a measure of the change in hydrogen concentration, are plotted in Fig. 3. Also shown is the function $c = A \exp - B(t - t_0)^2$, the values of A, B and t_0 being determined by the method of least squares. An alternative method is to treat t as the variate, and c as the frequency, so that $t_0 = \Sigma c_i t_i / \Sigma c_i$, and $1/2B = \Sigma c_i t_i^2 / \Sigma c_i - t_0^2$. This method is less accurate, but its advantage is that the standard deviation of B may be calculated without undue labour.

On applying these methods to calculate B, and getting the effective diffusion coefficient K from the relation $K = L^2/4^2 B$, we obtain the results shown in Table 2. L is the length of the pipe, 9,000 ft.

Table 2.

Run No.	10^{-5} R	10^3 c_f	U ft./sec.	$K/aU\sqrt{c_f}$ *from: Least squares*	*Frequency*	*Standard deviation %*
6	1·68	5·1	6·60	9·7	8·7	18
7	1·70	5·1	6·65	12·7	13·2	8
8	2·71	5·3	9·90	8·8	11·7	27

Volume injected

From the areas under the curves shown in Fig. 3, and the katharometer calibration, the volume of hydrogen injected in each case can be estimated.

The results were 8-10% greater than the values given by the pressure drop at the injection point. This discrepancy may be due to variation in the pipe diameter which could not, of course, be measured.

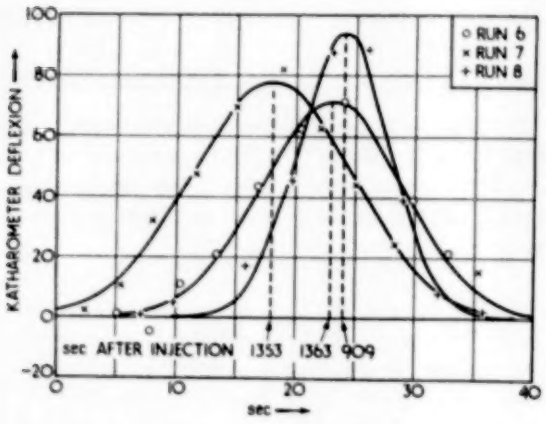

FIG. 3. Concentration of hydrogen at the outlet. The curves are fitted by the method of least squares.

DISCUSSION

The theoretical value of $K/aU\sqrt{c_f} = 7{\cdot}14$, given by TAYLOR [5] and previously verified only for liquids, is appreciably lower than the values shown in Table 2. However, the difference is of the same order as the standard deviations and we cannot conclude that there is a definite difference between gases and liquids, in view of the following uncertainties :

(i) The effect of the bends, 20 elbows at 90° and 8 at 45°, is uncertain. Although these bends account for only 5% of the pressure drop, it is impossible to be sure of the magnitude or the direction of their contribution to the longitudinal dispersion.

(ii) It is possible that some initial mixing may have been caused by the method of injection. The hydrogen was injected with the velocity of sound through a side tube, and this might distribute the gas over (say) a 20 ft. length instead of the 2 ft. assumed theoretically. The effective length of the slug at outlet was roughly 100 ft., so that an initial spread of 20 ft. would not be negligible.

CONCLUSIONS

It is certain that the effect of Schmidt number on longitudinal mixing is very much smaller than its effect on transfer to the walls. In the present case, using the commonly accepted factor $Sc^{0{\cdot}67}$ [4], the wall transfer coefficient would be 100 times higher for gases than for liquids. The widest variation that could be inferred from our results would be a factor of 2, and it seems more likely that there is a negligible difference between gases and liquids. This conclusion seems reasonable, since transfer to the walls involves molecular diffusion through the relatively stagnant boundary layer, while longitudinal transfer is brought about by a combination of the gradient of the mean velocity with mixing due to eddies.

Acknowledgement—The experimental work was done during a summer vacation course at the Stanlow Refinery of the *Shell Refining and Marketing Company*. The *Cabot Carbon Company* was also involved. We are indebted to both these Companies for their collaboration, and also to Mr. A. E. DISBREY of the Chemical Engineering Department, Cambridge, who constructed most of the apparatus.

NOTATION

A = peak deflexion of the katharometer
a = radius of the pipe
B = decay constant in $A \exp - B(t - t_0)^2$
c = concentration of hydrogen
c_f = pipe friction coefficient
D = molecular diffusivity
K = effective longitudinal diffusivity
L = length of pipeline
R = Reynolds number $= 2\rho Ua/\mu$
Sc = Schmidt number $\mu/\rho D$
t = time
μ = viscosity of line gas
ρ = density of line gas

Subscripts

0 = peak concentration
i = number of experimental point

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On the steady state fractionation of multicomponent and complex mixtures in an ideal cascade

Part 5. The extension to packed columns

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Summary—In previous papers the computations, both theoretical and numerical, involved in rectification for multicomponent and complex mixtures in cascades, were considered. The formulae may be extended to performance in packed columns so that the calculation of the number of transfer units for a given separation may be obtained with ease.

Résumé—Dans des articles précédents, les auteurs ont étudiés théoriquement et numériquement la rectification par plateaux des mélanges à plusieurs composants. Les résultats peuvent être étendus au cas des colonnes à garnissages de telle sorte que le calcul du nombre des unités de transfert pour une séparation donnée peut être obtenu facilement.

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MULTICOMPONENT SYSTEMS*

IF n is the number of transfer units and $y_n(i)$ and $y_n^*(i)$ is the vapour composition and the vapour composition which would be in equilibrium with the liquid, respectively, then the differential equation which describes the performance of a packed distillation column is

$$\frac{dy_n(i)}{dn} = y_n^*(i) - y_n(i) \tag{1}$$

As in previous parts the equilibrium relation will be assumed to be of the form

$$y_n(i) = \frac{\alpha(i)\,x_n(i)}{\sum_i \alpha(i)\,x_n(i)} \tag{2}$$

while the overall mass balance over the top n transfer units and total condenser is

$$y_n(i) = \frac{R}{R+1}x_n(i) + \frac{x_0(i)}{R+1} \tag{3}$$

UNDERWOOD [1] considered this system and his results will be rederived so that they may be more easily generalized to complex mixtures. Eqs. (1), (2) and (3) may be combined to give

$$\frac{R}{R+1}\frac{dx_n(i)}{dn} = \frac{\alpha(i)\,x_n(i)}{\sum_i \alpha(i)\,x_n(i)} - \frac{R}{R+1}x_n(i) - \frac{x_0(i)}{R+1} \tag{4}$$

It would be desirable to have formulae for the number of transfer units as a function of composition or for the change in composition as a function of the number of transfer units. With these ends in view a solution to Eq. (4) must be found.

Using the functions $v_k(i)$,

$$v_k(i) = \frac{p(i)}{\lambda_k - p(i)}$$

defined in Part 1, eq. (3·8), one may assume in order to find the solution that $x_n(i)$ can be expanded into a finite sum.

$$x_n(i) = x_0(i)\sum_k Q_k(n)\,v_k(i) \tag{5}$$

It follows that

$$Q_k(n) = C_k \sum_i \frac{x_n(i)}{\lambda_k - p(i)} \tag{6}$$

where :

$$C_k = \left[\sum_i \frac{x_0(i)\,p(i)}{[\lambda_k - p(i)]^2}\right]^{-1} \tag{7}$$

* Notation is as in Parts 1-4. See this journal.

from the orthogonality property of the set of $v_k(i)$. See Part 1, eqs. (3·8)–(3·11).

A summation of eq. (5) on i produces :

$$\sum_k Q_k(n) = \frac{1}{R}$$

so that eq. (4) may be written

$$\frac{R}{R+1}\sum_k \frac{dQ_k}{dn} v_k(i) = \frac{\alpha(i)\sum_k Q_k(n)\, v_k(i)}{\sum_k Q_k \sum_i \frac{x_0}{\lambda_k - p(i)}} - \frac{R}{R+1}\sum_k Q_k(n)\frac{\lambda_k}{\lambda_k - p(i)}$$

Now

$$\sum_i \frac{x_0}{\lambda_k - p(i)} = \sum_i \frac{x_0 p(i)}{p(i)\,(\lambda_k - p(i))} = \frac{R+1}{\lambda_k}$$

and

$$\sum_k \frac{dQ_k(n)}{dn} v_k(i) = \sum_k \frac{dQ_k(n)}{dn}\,[v_k(i) + 1] = \sum_k \left(\frac{dQ_k(n)}{dn} \cdot \frac{\lambda_k\, v_k(i)}{p(i)}\right)$$

since

$$\sum_k \frac{dQ_k(n)}{dn} = 0$$

Equating coefficients of $v_k(i)$ there results

$$R\frac{dQ_k(n)}{dn} = \frac{Q_k(n)}{\lambda_k \sum_k \frac{Q_k(n)}{k}} - RQ_k(n) \qquad (8)$$

Eq. (8) may be integrated between 0 and n to give

$$R \ln \frac{Q_k(n)}{Q_k(o)} = \frac{1}{\lambda_k}\int_0^n \frac{dn}{\sum_k \frac{Q_k(n)}{\lambda_k}} - Rn$$

The integral is a function of n alone and may be written $f(n)$ so that

$$\lambda_k \ln \frac{Q_k(n)}{Q_k(o)} + n\lambda_k = f(n) \qquad (9)$$

Thus if one considers two different k's say k and j, then the function $f(n)$ need not be computed at all since one can easily show that

$$n = \frac{1}{\lambda_j - \lambda_k} \ln \left[\frac{Q_k(n)}{Q_k(o)}\right]^{\lambda_k} \left[\frac{Q_j(o)}{Q_j(n)}\right]^{\lambda_j} \qquad (10)$$

Note that this formula gives the number of transfer units in terms of readily calculable quantities. The $Q_k(n)$ are computed from eq. (7) and the λ_k from

$$\sum_i \frac{p(i)\, x_0(i)}{\lambda_k - p(i)} = R$$

also

$$Q_k(o) = \frac{R+1}{\lambda_k} C_k$$

Hence

$$n = \frac{1}{\lambda_j - \lambda_k} \ln \frac{\lambda_k}{k}^{\lambda_k} \Big/ T_j^{\lambda_j}$$

with

$$T_k = \frac{\lambda_k}{R+1}\sum_i \frac{x_n(i)}{\lambda_k - p(i)}$$

Complex Mixtures

In complex mixtures it is clear that eqs. (1) and (3) still hold with $x_n(i)$ and $y_n(i)$ as distribution functions. Eq. (2) requires appropriate modification with the summation replaced by an integral. The limiting process may now be applied to the multicomponent case in the same fashion as was done in Part 1. It is clear that the functions $\rho(\lambda)$ and $w(\lambda)$ may be defined as before to give

$$\lambda\, x_0(\lambda)\, \pi \cot \pi\rho(\lambda) = R - P\int_0^\infty \frac{q\, x_0(q)}{\lambda - q}\, dq = w(\lambda) \qquad (11)$$

where $x_0(\lambda)$ is the distribution function of the overhead product.

Eq. (6) and (7) then become on passing to the limit

$$Q(\lambda, n) = C(\lambda)\left[P\int_0^\infty \frac{x_n(q)}{\lambda - q}\, dq + x_n(\lambda)\, \pi \cot \pi\rho(\lambda)\right] \qquad (12)$$

and

$$C(\lambda) = \frac{\lambda x_0(\lambda)}{w^2(\lambda) + [\pi\lambda\, x_0(\lambda)]^2} \qquad (13)$$

while from eq. (5)

$$x_n(p) = px_0(p) \left[P \int_0^\infty \frac{Q(\lambda,n)}{\lambda - p}\, d\lambda + Q(\lambda,n)\, \pi \cot \pi\rho(p) \right]$$

Note that $Q(\lambda, n)$ depends upon the distribution function at two points within the column, for $x_n(q)$ occurs explicitly in eq. (12) while $x_0(\lambda)$ occurs in eq. (13). The limiting process used in Part 1 then may be extended to eq. (9) to give

$$\lambda \ln \frac{Q(\lambda,n)}{Q(\lambda,o)} + n\lambda = F(n)$$

If two different values of λ are chosen, say λ and γ, then

$$n = \frac{1}{\gamma - \lambda} \ln \left[\frac{Q(\lambda,n)}{Q(\lambda,o)} \right]^\lambda \left[\frac{Q(\gamma,o)}{Q(\gamma,n)} \right]^\gamma \qquad (14)$$

Thus one may compute the number of transfer units required for a given separation provided the two compositions are known in detail. The problem would generally not be stated in this form and a trial and error procedure of the usual kind would be required for other cases.

Eq. (14) may be simplified somewhat for

$$Q(\lambda,o) = C(\lambda) \left[P \int_0^\infty \frac{x_0(q)}{\lambda - q}\, dq + x_0(\lambda)\, \pi \cot \pi\rho(\lambda) \right] = C(\lambda) \frac{R+1}{\lambda}$$

Therefore, if,

$$S(\lambda,n) = \frac{Q(\lambda,n)}{Q(\lambda,o)} = \frac{\lambda}{R+1} \left[P \int_0^\infty \frac{x_n(q)\, dq}{\lambda - q} + x_n(\lambda)\, \pi \cot \pi\rho(\lambda) \right]$$

$$n = \frac{1}{\gamma - \lambda} \ln \frac{[S(\lambda,n)]^\lambda}{[S(\gamma,n)]^\gamma}$$

This formula is much better from the point of view of computation. It should be pointed out that the integrals appearing here although written from 0 to ∞ are not really improper at either end since relative volatilities are not zero or infinite. The integrals are improper at $\lambda = p$, however, and the computations require the Cauchy principle values. The computation of such integrals was discussed in Part 3.

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Mixing by agitation of miscible liquids

Part II

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3.5. *Power consumption*

THE power consumption was measured as described in chapter 2.2.

The abundance of data given in literature on the power consumption of stirrers made it superfluous to investigate this point extensively. We, therefore, only measured the power consumption of stirrers under conditions not yet, or not adequately, dealt with in the literature. In this way various stirring conditions on a basis of mixing time and power consumption can be compared (chapter 4).

The power consumption P was converted in the usual way into the dimensionless group $\frac{P}{\rho n^3 d^5}$, which was then correlated with the other dimensionless groups, such as Reynolds number $\frac{\rho n d^2}{\mu}$ and various length ratios. These correlations are of an experimental nature. It was not possible to establish a relationship between power consumption of the stirrer and mixing time. The two quantities are more or less independent of each other. Depending on stirring conditions, it is possible to obtain several mixing times at a given power consumption of the stirrer. Naturally, the shortest mixing time is generally to be preferred.

Paddle stirrer—A large amount of data on this type of stirrer can be found in the literature. WHITE and his collaborators found the following experimental correlation [18].

$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-0.14} \left(\frac{d}{D}\right)^{-1.7} \left(\frac{w}{d}\right)^{0.3} \left(\frac{H}{D}\right)^{0.6}$$

MILLER and MANN [12] found the following relations :

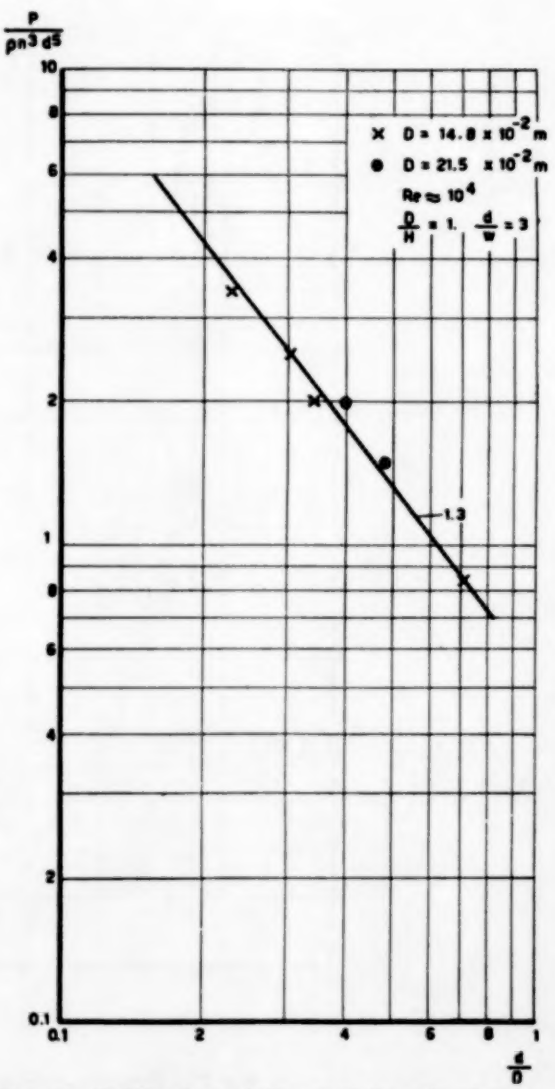

FIG. 16. Paddle stirrer. Influence of the ratio stirrer to vessel diameter on the dimensionless power consumption.

$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-0.22} \left(\frac{H}{D}\right)^{0.66},$$

(in which only n and H were varied). This expression holds true for paddle stirrers with a blade angle of $\alpha = 90°$ as well as for paddle stirrers with a blade angle of $\alpha = 45°$. The proportionality constant is different in both cases.

From the survey given by HOOKER [7] it follows that

$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-0.2} \left(\frac{d}{D}\right)^{-1.4} \left(\frac{H}{D}\right)^{0.62} \left(\frac{w}{d}\right)^{0.5}$$

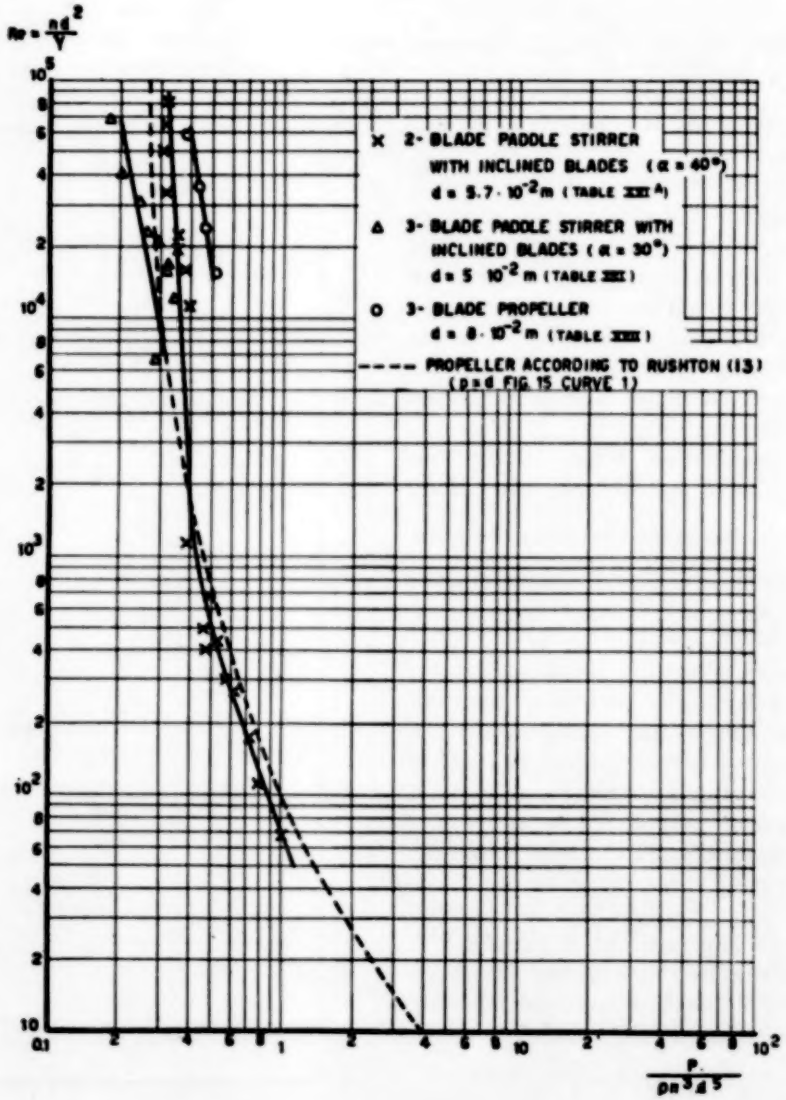
Re = nd²/ν
× 2- BLADE PADDLE STIRRER WITH INCLINED BLADES (α = 40°) d = 5.7 · 10⁻²m (TABLE XXII A)
△ 3- BLADE PADDLE STIRRER WITH INCLINED BLADES (α = 30°) d = 5 10⁻²m (TABLE XXII)
○ 3- BLADE PROPELLER d = 8 · 10⁻²m (TABLE XXIII)
---- PROPELLER ACCORDING TO RUSHTON (13) (p = d FIG 15 CURVE 1)
P/ρn³d⁵

FIG. 17. Propeller stirrer and paddle stirrer with inclined blades. Influence of Reynolds number on dimensionless power consumption.

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From our own investigations we found the expression

$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-0.15} \left(\frac{d}{D}\right)^{-1.3} \qquad \text{(Figs. 16, 17)}$$

The influence of $\frac{H}{D}$ and $\frac{w}{d}$ was not further ascertained as these quantities have already been sufficiently studied. Hence, the following formula may be used with a fair amount of reliability for the power consumption of paddle stirrers :

$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-0.15} \left(\frac{d}{D}\right)^{-1.3} \left(\frac{H}{D}\right)^{0.6} \left(\frac{w}{d}\right)^{0.4} \qquad (3)$$

These formulae only apply in the turbulent region, i.e. for $Re > 10^3$ to 10^4.

For $Re < 10^2$ to 10^3 the flow becomes laminar, as was already found in the measurements of the mixing time. In this region

$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-1}$$

Turbomixers—The relations holding for paddle stirrers also apply in the case of turbomixers.

For turbomixers Mack [11] found the following complicated relation in the turbulent region

$$\frac{P}{\rho n^3 d^5} = 9{\cdot}74\, s^{0.495} \left(\frac{w}{d}\right)^{1.33 s^{-0.108}}$$

For practical use the formula may be simplified to

$$\frac{P}{\rho n^3 d^5} = 9{\cdot}7\, s^{0.5} \left(\frac{w}{d}\right)^{1} \quad (s = \text{number of vanes})$$

The influence of the Reynolds number was negligible owing to the presence of stator rings.

To ascertain what happens to the power consumption when the paddle stirrer is changed into a turbomixer the influence of vane angle β on power consumption was measured. The relation can be represented by the formula

$$\frac{P}{\rho n^3 d^5} \sim (\sin \beta)^{0.23}$$

This relation was ascertained for the turbulent region.

Propeller stirrers and paddle stirrers with inclined blades ($\alpha < 90°$). The formula (3) is also more or less applicable to propeller stirrers.

Measurements by Stoops and Lovell [16] produced the following result :

$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-0.2} \left(\frac{d}{D}\right)^{-0.9}$$ (in these measurements only n and d were varied)

The diameter remaining the same, the power consumption increases about proportionately to the pitch of the propeller [13]. Only few reliable measurements on this point have been recorded. For paddle stirrers the influence of the blade angle α on the power consumption was ascertained (Fig. 18). It was found that

$$\frac{P}{\rho n^3 d^5} \sim (\sin \alpha)^{\sim 2.5}$$

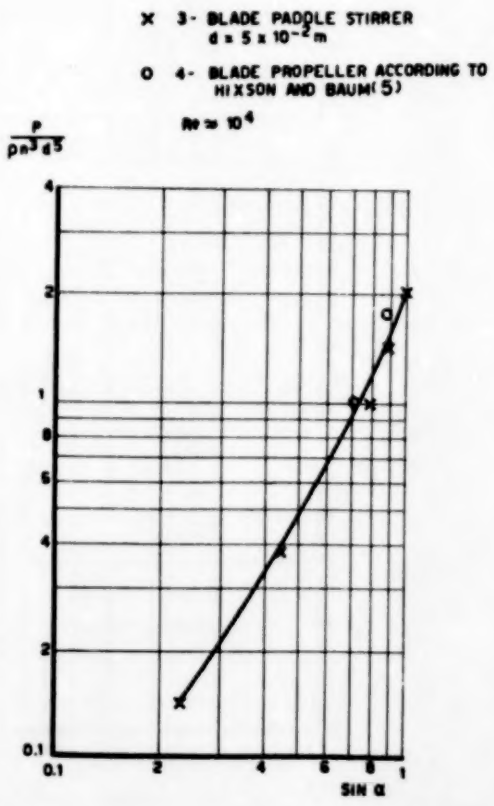

Fig. 18. Paddle stirrer with inclined blades. Influence of blade angle α on the dimensionless power consumption.

The relation between power consumption and Reynolds number is shown in Fig. 17. It is in good agreement with that for propellers, as given by RUSHTON [18]. No baffles were used in any of these experiments.

Baffling, eccentricity of stirrer—If the mixing vessel is fitted with baffles (see Fig. 1A), or if a turbomixer has a stator ring round the turbine wheel the influence of Reynolds number on the power number is almost nil. The power consumption increases by a factor of from 2 to 5 (Fig. 19) when using baffles.

Eccentricity of the stirrer has about the same effect on the power consumption as has baffling. Measurements on paddle stirrers showed an increase in power consumption by a factor of

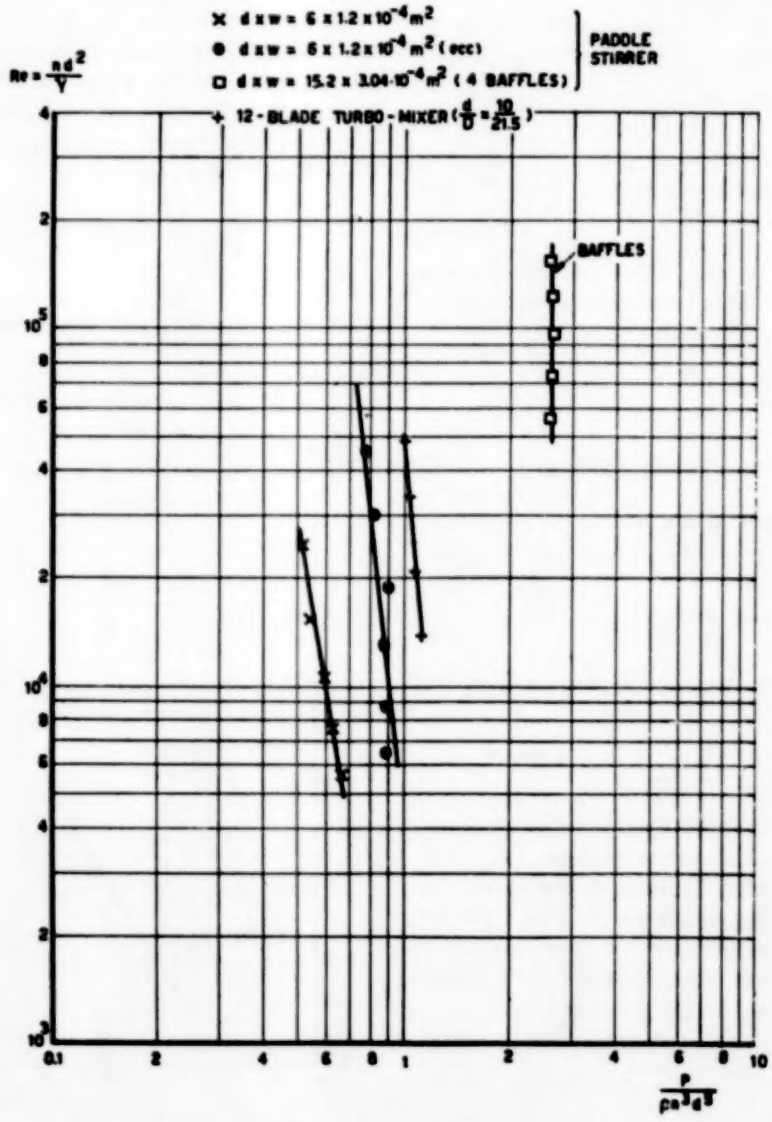
× d x w = 6 x 1.2 x 10⁻⁴ m²
● d x w = 6 x 1.2 x 10⁻⁴ m² (ecc)
□ d x w = 15.2 x 3.04·10⁻⁴ m² (4 BAFFLES)
PADDLE STIRRER
+ 12-BLADE TURBO-MIXER (d/D = 10/21.5)
Re = nd²/ν
BAFFLES
P/ρn³d⁵

FIG. 19. Paddle stirrer and turbomixer. Influence of Reynolds number on dimensionless power consumption.

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from 1·5 to 2·5, this increase being 1 to 1·5 in the case of propeller stirrers ($e = 0{\cdot}5$).

3.6. *Mixing energy*

Multiplication of the mixing time by the power consumption of the stirrer yields the energy consumed for complete mixing.

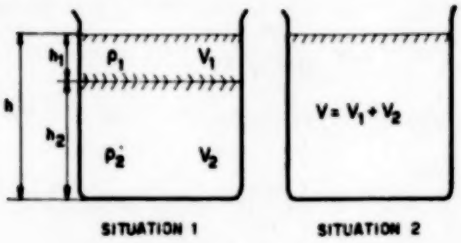

FIG. D

The theoretical minimum of mixing energy required can be calculated as follows (see figure). In situation 1 the potential energy of the two liquid layers with respect to the bottom of the vessel is :

$$E_{pot_1} = V_1 \rho_1 g (h_2 + \tfrac{1}{2}h_1) + V_2 \rho_2 g (\tfrac{1}{2}h_2).$$

In situation 2 the potential energy is equal to :

$$E_{pot_2} = (V_1 + V_2)\left(\frac{\rho_1 V_1 + \rho_2 V_2}{V_1 + V_2}\right) g. \tfrac{1}{2}(h_1 + h_2).$$

The increase in potential energy becomes :

$$E = E_{pot_2} - E_{pot_1} = \tfrac{1}{2} V_1 h_2 (\rho_2 - \rho_1) g$$

$$\text{if } \frac{V_1}{V} = \phi \; E = \tfrac{1}{2}\phi (1 - \phi) \; Vh (\rho_2 - \rho_1) g.$$

The increase E represents the theoretical minimum of mixing energy required. It can reach a maximum of $0{\cdot}125 \; Vh (\rho_2 - \rho_1) g$. In that case $\phi = \frac{1}{2}$, i.e. the two liquid volumes V_1 and V_2 are equal to each other. In our experiments this is the normal case. We found that this theoretical mixing energy is only a small percentage of the mixing energy actually required.

4. Discussion of Optimum Stirring Conditions

4.1. *Conditions for optimum performance (efficiency)*

With the correlations found for mixing time and power consumption optimum conditions can be derived for the dimensions and shape of stirrer and vessel.

The optimum stirring conditions may, among other things, be defined as :

(*a*) those in which the power consumption is lowest for a specified mixing time ;

(*b*) those in which the mixing time is shortest for a specified power consumption.

The data will be analysed according to the first definition. However, we would add that an analysis based on the second definition in most cases leads to the same results.

For a given mixing process the physical properties of the liquid are, of course, fixed. The shape and dimensions of stirrer and vessel are generally, within certain limits. left to the designer. When these variables, too, have been established, the speed of rotation must be such as will ensure mixing within the required time.

For the mixing time T we may write :

$$T = T\left(n, \frac{d}{D}, V, \frac{H}{D}, \frac{w}{d}, \alpha, \beta\right)$$

and for the power consumption P :

$$P = P\left(n, \frac{d}{D}, V, \frac{H}{D}, \frac{w}{d}, \alpha, \beta\right)$$

We will successively deal with the influence of the volume of the mixing vessel V ;

the stirrer diameter ratio $\frac{d}{D}$;

the height ratio of the liquid in the vessel $\frac{H}{D}$;

the width ratio of the stirrer blade $\frac{w}{d}$;

blade angle α ;

vane angle β.

The procedure for determining the optimum conditions consists in varying n and only one of the other variables, the remaining ones being kept constant. For a constant mixing time the variation of n depends on that of the variable that has not been kept constant. In this way the value at which power consumption is lowest can be determined for any of the variables involved : Because

of the special structure of the formulae for T and P the optimum value found for one variable is little influenced by even quite considerable changes of the other variables.

4.2. *Influence of liquid volume* V *in mixing vessel*

If $\tau \sim \left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right)^{-0.3}$ and, moreover, T does not depend on the Reynolds' number equation (2) may be written as $T \sim n^{-1} (n^2 d)^{-0.3}$, while equation (3) becomes $P \sim n^3 d^5 (nd^2)^{-0.15}$.

Elimination of n gives :

$$P \sim T^{-1.78} d^{4.17} \quad \text{or}$$

$$P \sim T^{-1.78} V^{1.4} \quad (\text{as } d^3 \sim V)$$

Power consumption per unit volume, P/V, is proportional to $T^{-1.78} V^{0.4}$ and therefore increases when the liquid volume increases (no optimum). The mixing energy per unit volume, $\frac{PT}{V}$, which is proportional to $T^{-0.78} V^{0.4}$, also increases at higher V values as well as at smaller T values.

When the quantity $\frac{\rho n^2 d^2}{\Delta \rho g H}$ has no influence on τ, $P \sim T^{-2.85} V^{1.6}$ and therefore $\frac{PT}{V} \sim T^{-1.85} V^{0.6}$. It is therefore advantageous to use a small mixing vessel. In large vessels several small stirrers pumping in the same direction are to be preferred to one large stirrer.

4.3. *Influence of stirrer and vessel dimensions*

4.3.1. *Influence of the stirrer/vessel diameter ratio* $\frac{d}{D}$ $\left(\frac{H}{D}$ *and* D^2H *are constant*$\right)$

The equation for T becomes :

$$T \sim n^{-1.6} d^{-3.6} f\left(\frac{d^3}{D^{2.5} H^{0.5}}\right) \qquad (Re > 10^4)$$

where $f\left(\frac{d^3}{D^{2.5} H^{0.5}}\right)$ is given by Fig. 9, and equation (3) becomes

$$P \sim n^{2.85} d^{4.4} \left(\frac{d}{D}\right)^{-1.3}$$

For $\frac{d^3}{D^{2.5} H^{0.5}} < 0.04$ $f\left(\frac{d^3}{D^{2.5} H^{0.5}}\right) = \text{constant}$. For the mixing time T it is then true that $T \sim n^{-1.6} d^{-3.6}$. Furthermore, $P \sim n^{2.85} d^{3.1}$. Elimination of n produces $P \sim T^{-1.78} d^{-3.4}$. For a given time T the power consumption will decrease as the stirring diameter increases. Hence, the best plan will be to take the largest possible diameter. For $\frac{d^3}{D^{2.5} H^{0.5}} > 0.08$ it is true that $f\left(\frac{d^3}{D^{2.5} H^{0.5}}\right) \sim \frac{d^3}{D^{2.5} H^{0.5}}$. The mixing time T becomes :

$$T \sim n^{-1.6} d^{-3.6} \left(\frac{d}{D}\right)^3 \quad \text{or} \quad T \sim n^{-1.6} d^{-0.6}$$

$$\text{and} \qquad P \sim n^{2.85} d^{4.4} \left(\frac{d}{D}\right)^{-1.3}$$

Elimination of n produces :

$$P \sim T^{-1.78} d^{3.4} \left(\frac{d}{D}\right)^{-1.3} \quad \text{or} \quad P \sim T^{-1.78} d^{2.0}.$$

In this region P will increase with increasing stirrer diameter if T is kept constant. The best plan is then to keep the stirrer diameter as small as possible.

There is, therefore, an optimum diameter in the region :

$$0.04 < \frac{d^3}{D^{2.5} H^{0.5}} < 0.08 \text{ or } 0.34 < \left(\frac{d}{D}\right)\left(\frac{H}{D}\right)^{1/6} < 0.43.$$

Practically speaking, this means that this diameter corresponds with a value of $\frac{d}{D} \approx 0.4$, as the value of $\left(\frac{D}{H}\right)^{1/6}$ in most cases will not differ very much from 1.

The above results are only valid for a turbulent field of flow. In the laminar range ($Re < 250$) the mixing time very rapidly increases at lower Reynolds' values (Figs. 7 and 8). In this case it is better to take the largest possible stirrer diameter, as will be shown below. In this region it has been assumed that :

$$\frac{Tnd^3}{V} \left(\frac{\rho n^2 d^2}{\Delta \rho g H}\right)^{0.3} \sim \left(\frac{\rho n d^2}{\mu}\right)^{-3} \cdot f\left(\frac{d^3}{D^{2.5} H^{0.5}}\right),$$

and :

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$$\frac{P}{\rho n^3 d^5} \sim \left(\frac{nd^2}{\nu}\right)^{-1} \cdot \left(\frac{d}{D}\right)^{-1.3}$$

If $f\left(\frac{d^3}{D^{2.5}H^{0.5}}\right) = \left(\frac{d}{D}\right)^3$ $\left[\left(\text{for } \frac{d^3}{D^{2.5}H^{0.5}}\right) > 0.08 \text{ and } \frac{H}{D} = \text{constant}\right]$, we find :

$$P \sim T^{-0.44}\, d^{-1.1},$$

which proves that here a large diameter is favourable. In actual practice the stirrer diameter will have to be about equal to the vessel diameter when mixing viscous liquids.

4.3.2. *Influence of liquid height* $\frac{H}{D}$ $\left(\frac{d}{D}\right.$ and D^2H are constant$\left.\right)$

In the same way as shown in the preceding section the influence of $\frac{H}{D}$ can be found. From equation (2) it follows that $T \sim n^{-1} d^{-3} \left(\frac{n^2D^2}{H}\right)^{-0.3} f\left(\frac{H}{D}\right)$, while from equation (3) it is found that $P \sim n^3 d^5 (nd^2)^{-0.15} \left(\frac{H}{D}\right)^{0.6}$. Elimination of n now (D^2H is constant) gives the following relation : $P \sim T^{-1.8} H^{1.22} \left\{f\left(\frac{H}{D}\right)\right\}^{1.8}$. For $\frac{d^3}{D^{2.5}H^{0.5}} < 0.05$, $f\left(\frac{H}{D}\right) = \text{constant}$, so that then $P \sim T^{-1.8} H^{1.22}$.

In other words, P increases with increasing H values.

For $\frac{d^3}{D^{2.5}H^{0.5}} > 0.05$, $f\left(\frac{H}{D}\right) = \left(\frac{H}{D}\right)^{-0.5}$ and as $D \sim H^{-0.5}$, $P \sim T^{-1.8} H^{1.22-1.35} = T^{-1.8} H^{-0.13}$. Hence, in this region P slightly decreases with increasing H values. There is therefore an optimum value for $\frac{a^3}{D^{2.5}H^{0.5}} = 0.05$. When $\frac{d}{D}$ is taken equal to 0·4 the value for $\frac{H}{D}$ proves to become ≈ 0.8, which is a normal charge depth in actual practice.

4.3.3. *Width of stirrer blade* $\left(\text{influence of } \frac{w}{d}\right)$

From the formula for power consumption and mixing time, giving the influence of the width of the stirrer, we may derive rules for the most favourable dimensions of the stirrer.

From eq. (3) it can be derived that $\frac{P}{\rho n^3 d^5} \sim \left(\frac{w}{d}\right)^{0.4}$, while $T \sim (nd^2w)^{-1}$ holds good (if $\frac{w}{d} < 0.5$), when the Froude number has no influence. Elimination of n gives $P \sim T^{-3} w^{-2.6}$. Hence, $P \sim w^{-2.6}$ for T = constant.

According to this formula the blade should be made as wide as possible.

For values of $\frac{w}{d} > 0.5$, $T \sim (nd^2w)^{-1} \left(\frac{w}{d}\right)^{0.66}$ (see section 3.2.1), hence, $T \sim n^{-1} w^{0.33}$. For the power consumption P we find after elimination of n : $P \sim T^{-3} w^{-0.6}$.

Thus, for $\frac{w}{d} > 0.5$ there is still a small effect of $\frac{w}{d}$ on the efficiency. In practice the ratio $\frac{w}{d} = 0.5$ is never exceeded.

When the density Froude number exerts an influence we obtain for

$$\frac{w}{d} < 0.5 \quad P \sim T^{-1.9} w^{-1.5}$$

$$\frac{w}{d} > 0.5 \quad P \sim T^{-1.9} w^{-0.2}$$

i.e., the trend remains the same.

4.4. *Type of stirrer*

4.4.1. *Influence of blade angle* α

The value of the blade angle α more or less determines the type of stirrer (paddle or propeller) and the influence of α shows which type of stirrer is the most effective. From the relation found between mixing time and blade angle it can be ascertained what blade angle is most suitable.

$$T \sim n^{-1.6} (\sin \alpha)^{-k_1} \quad k_1 = 1 \text{ to } 2$$

$$P \sim n^{2.85} (\sin \alpha)^{k_2} \quad k_2 = 2 \text{ to } 3$$

Elimination of n produces

$$P \sim T^{-1.78} (\sin \alpha)^{k_2 - 1.7 k_1}$$

For constant mixing time T, P varies according to $P \sim (\sin \alpha)^{k_2 - 1{\cdot}7\,k_1}$. For $(k_2 - 1{\cdot}7\,k_1) > 0$, P increases with $\sin \alpha$; for $(k_2 - 1{\cdot}7\,k_1) < 0$ it decreases with $\sin \alpha$. From Figs. 14 and 18, k_2 and k_1 for various values of α may be found.

For $0° \leqslant \alpha \leqslant 45°$, $k_1 \approx 1$ and $k_2 \approx 1{\cdot}5$, so that $k_2 - 1{\cdot}7\,k_1 \sim -0{\cdot}2$. For $45° \leqslant \alpha \leqslant 90°$, $k_1 \approx 2$ and $k_2 \approx 2{\cdot}4$; then $k_2 - 1{\cdot}7\,k_1 \sim 0$.

The small values found for $k_2 - 1{\cdot}7\,k_1$ make it clear that the influence of α is only very small; in other words, the propeller stirrer has about the same performance as the paddle stirrer.

4.4.2. *Influence of vane angle β*

The influence of the vane angle decides whether a paddle ($\beta = 90°$) or a turbomixeir ($\beta < 90°$) is to be preferred. The equation for the mixing time in this case becomes:

$$T \sim n^{-1{\cdot}6}\,(\sin \beta)^{-1}$$

and the equation for the power consumption:

$$P \sim n^{+2{\cdot}85}\,(\sin \beta)^{0{\cdot}23}.$$

Therefore, $P \sim T^{-1{\cdot}8}\,(\sin \beta)^{-1{\cdot}6}$.

Hence, a high $\sin \beta$ value is favourable for mixing; in other words, the paddle mixer is more efficient than the turbomixer.

4.5. *Comparison with jet mixing*

Jet mixing with external circulation of liquid is frequently applied in industry. An important point is the size of the nozzle. FOSSETT and PROSSER [4] investigated into the possibilities of jet mixing and derived an expression for the mixing time. This enables us to compare jet mixing with mixing by agitation by extrapolation of the large-scale results of FOSSETT and PROSSER to our small-scale experiments. The basis of comparison is again power consumption with equal mixing times (see Fig. 20).

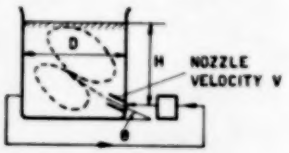

FIG. E

The velocity of the liquid v at the nozzle must comply with the condition $\frac{v^2}{2g} = k\,\frac{H\,(\rho_1 - \rho_2)}{\rho_2 \sin^2 \theta}$ (4), where k is a constant still dependent on $\frac{\rho_2 - \rho_1}{\rho_2}$ $\left[k \sim \left(\frac{\rho_2 - \rho_1}{\rho_2}\right)^{-0{\cdot}3}\right]$. For $\frac{\rho_2 - \rho_1}{\rho_2} = 0{\cdot}079$, $k = 14$, $H = 118$ mm. Let $\sin \theta$ be $= \frac{1}{2}\sqrt{2}$, then $\frac{v^2}{2g} = 0{\cdot}26$ m and $v = 2{\cdot}30$ m/sec. The mixing time T can be found from $T = \frac{8D^2}{\sqrt{Qv}}$. For $D = 148$ mm. $T = 0{\cdot}120\,Q^{-0{\cdot}5}$ sec (Q in m³/sec).

The required power input is found from $P = \frac{1}{2}\,\rho\,v^2 \times Q = 2{\cdot}6 \times 10^{+3}\,Q$ Nm/sec. Fig. 20 gives the P and T values corresponding to various Q values. It will be seen that the power consumption in jet mixing is about four times as high as in paddle mixing. With the aid of a P/V vs. T graph (Fig. 20) an adequate comparison between

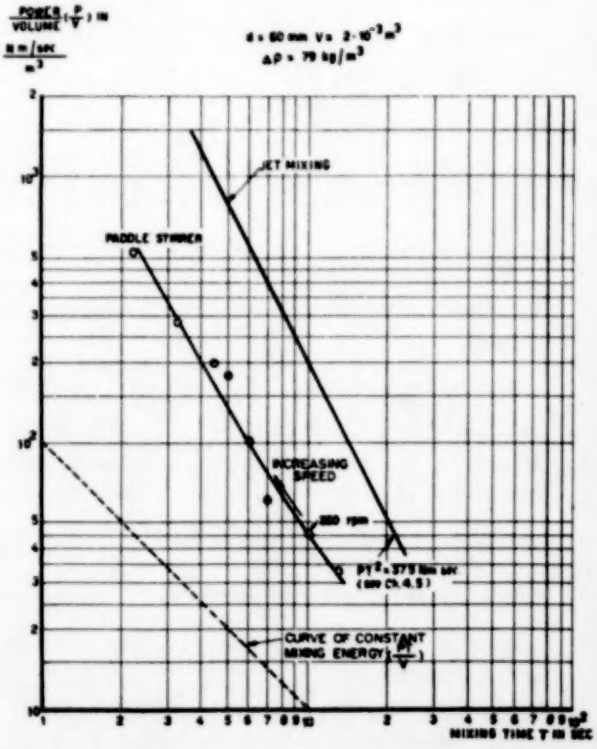

FIG. 20. Comparison between jet mixing and paddle stirrer.

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various stirring devices can be reached. Elimination of Q gives $PT^2 = 37{\cdot}5$ Nm sec.

4.6. *Concluding remarks*

A general survey of the efficiency of the various types of stirrers, using the optimum stirrer dimensions, is given in the table below.

5. Continuous Mixing of Liquids

5.1. *Introduction*

Continuous mixing of liquids is understood to be the operation where one or more streams of liquid are continuously fed into and discharged from a mixing vessel. Both the flow rates and the compositions of the liquids may vary with time. The flow rate at the outlet will at any time be equal to the sum of the flow rates of the inflowing streams; the final composition will be a function of the flow rates and compositions of the inflowing liquids and of the degree of mixing in the mixing vessel.

Mixing in the mixing vessel is called perfect (one ideal mixing stage) if the inflowing liquids are immediately and completely mixed with the fluid in the vessel, so that its properties are uniform and identical with those of the outgoing stream. This case is frequently encountered in the literature and calculations on stirred reactors are often based on this assumption.

Complete absence of mixing occurs if the elements of the entering liquid move through the vessel at constant and equal velocities along parallel paths, so that no mixing takes place either in the direction of flow or in other (radial) directions.

The case of no mixing in the directions of flow (perfect piston flow) can be approached by an infinite number of ideal mixing stages lined up in series.

The normal case of a non-perfect mixer is very difficult to handle mathematically. The conception of an eddy diffusivity in axial and (or) in radial direction as usually applied in packed beds and in particulate fluidized beds, does not hold for the case of an agitated vessel.

The continuous-flow mixing of one liquid stream can be suitably characterized by the curve of the outlet concentration against time, if the inlet concentration is a well-defined function of time (e.g. a step function).

In many processes two liquid streams with constant concentrations must be mixed. In this particular case only mixing in a radial direction is important, which can be effected, for instance, by line blending. As a rule, the liquid will be uniform after having passed through a pipe length of about thirty times the pipe diameter (turbulent flow conditions). Bends and constrictions appreciably improve mixing.

To conclude our investigation, a few experiments were performed with one liquid stream to evaluate the relation between batch mixing and continuous mixing.

5.2. *Measurements (mixing times)*

The experiments were carried out in a mixing vessel ($H = D = 0{\cdot}15$ m) with a centrally placed stirrer (Fig. 21A). In order to obtain an even distribution of the inflowing liquid stream the vessel was provided with an inlet compartment

Comparison of some types of stirrer on a basis of power consumption (in arbitrary units) required to ensure a certain mixing time T			*Optimum dimensions of stirrer*
Paddle stirrer	no baffles	100	V as small as possible
Turbomixer	no baffles	170	$\frac{d}{D} = 0{\cdot}4$
Propeller stirrer	no baffles	100	$\frac{H}{D} = 0{\cdot}8$
Jet mixing		400	$\frac{w}{d} = 0{\cdot}5$
			$\beta = 90°$

consisting of perforated plates with the same diameter as the vessel. In this way mixing caused by the injection of the fluids was suppressed. Disturbance of the flow pattern by the outlet was avoided by using a sieve bottom.

As the sole object of this investigation was the study of stirrers, the influence of different types of inlet nozzles, etc., was not further examined.

A small amount of dye solution (bromophenol blue) was instantaneously injected into the inflowing liquid stream (10 ml in 1 sec). The distribution of the colour through the mixing vessel and in the outgoing streams (under the sieve bottoms) was watched. The outlet concentration curves for an ideal mixer and a completely non-ideal mixer are given in Fig. 21B (curves 1 and 2).

The outlet concentration will show a maximum, which in the normal case of a non-perfect mixer will appear a time T after the moment of dye injection, which time is shorter than the residence time $\left(\frac{\text{volume of vessel}}{\text{flow rate}}\right)$ (Fig. 21B, curve 3).

In most experiments an even colour distribution throughout the vessel could be observed some time after the injection (2), which " mixing time " corresponds to the time T. The piston flow mixer (Fig. 21B, curve 2) will, of course, never give such a " mixing time."

The mixing times T were measured as a function of agitator speed and flow rate. The influence of the flow rate on T in the case of a stagnant stirrer is shown in Fig. 22. The times then found (called T_2) are always shorter than the residence times (T_R). The value of $\frac{T_2}{T_R}$ will, of course, depend on the conditions of flow in the mixing vessel, hence, on the construction of the inlet, channeling effects, etc.

The influence of the stirrer speed on the mixing time T when there is no flow is the same as in batch mixing (mixing time T_1).

In the case of both liquid flow and stirring the mixing times T appear to correlate with the batch mixing time T_1 and the time T_2, as is shown in Fig. 23. The best correlation for T in terms of T_1 and T_2 is given by $\frac{1}{T} = \frac{1}{T_1} + \frac{1}{T_2} + \frac{0{\cdot}5}{\sqrt{T_1\,T_2}}$.

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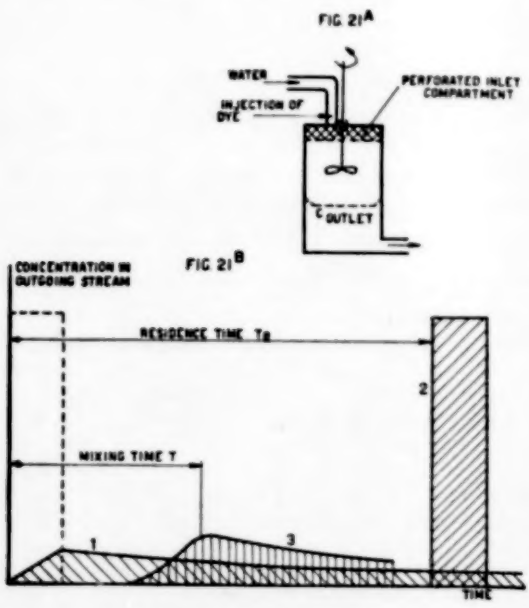

FIG. 21. Continuous mixing.

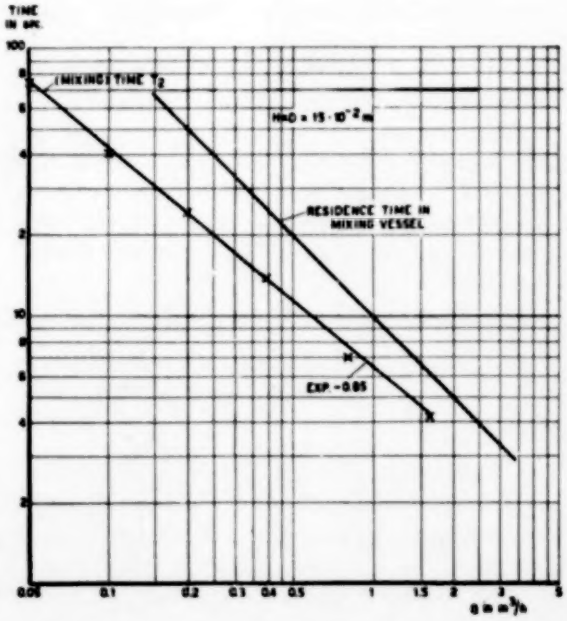

FIG. 22. Continuous mixing. (Mixing) time T_2 vs. flow rate Q (no stirring).

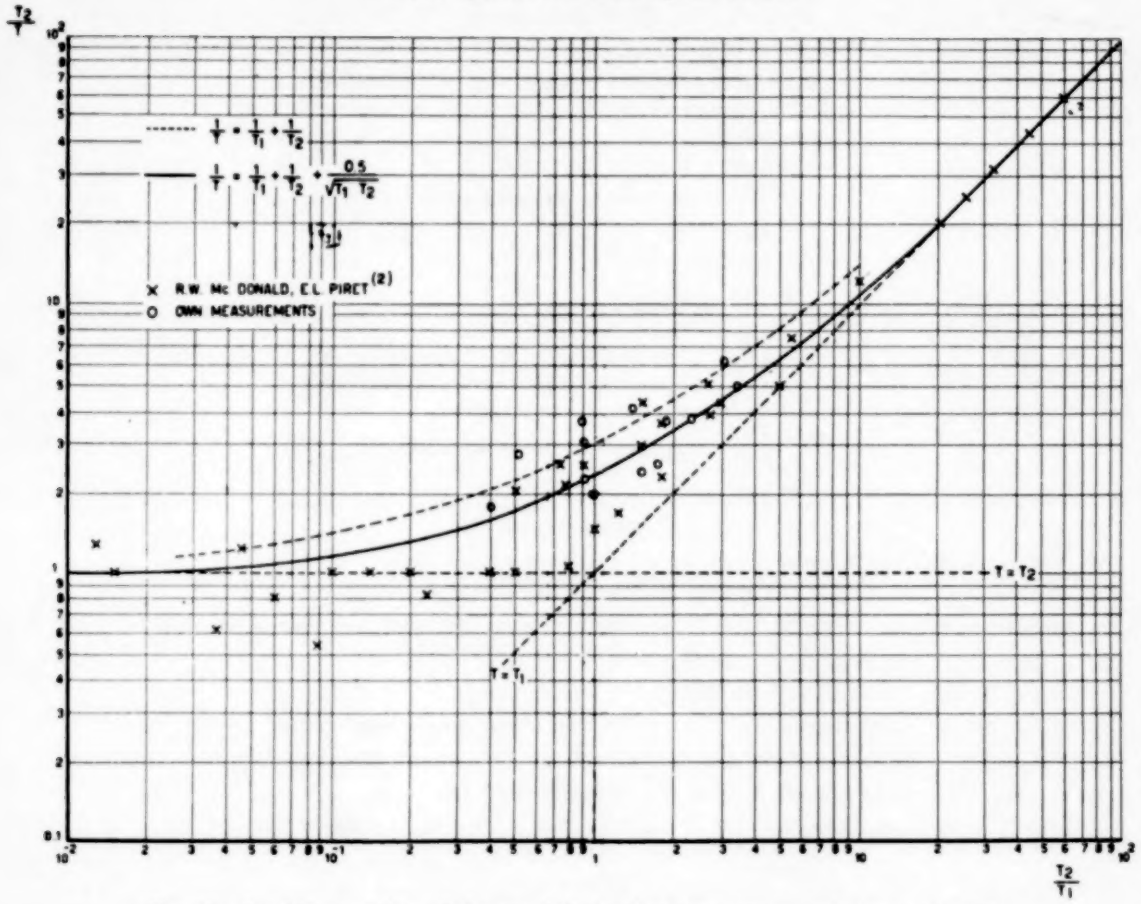

FIG. 23. Continuous mixing. Influence of the batch mixing time T_1 (only due to stirring) and the (mixing) time T_2 (only due to the flow) on the mixing time T (stirring and flow).

Summarizing our results, it may be said that in the case of continuous flow through a stirred vessel the mixing time T can be predicted from the mixing time in batch operation (T_1) and a time T_2, which is always shorter than the residence time.

If the batch mixing time $T_1 \leqslant T_R$, then $T \leqslant T_R$, in which case a perfect mixer is approached.

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NOTATION

		Units
d	= stirrer diameter	m
D	= vessel diameter	m
e	= eccentricity of stirrer	
g	= acceleration of gravity	m/sec^2
H	= height of liquid in vessel	m
n	= number of revolutions of stirrer per unit time	sec^{-1}
n_D	= refractive index	
p	= pitch of propeller stirrer	m
P	= power consumption	Nm/sec
Q	= pumping capacity	m^3/sec
r	= radius	m
s	= number of vanes (or blades)	
T	= mixing time	sec
v	= velocity	m/sec
V	= liquid volume in mixing vessel	m^3
w	= width of stirrer blade	m
α	= blade angle (paddle with inclined blades)	

	Units
β = vane angle (turbomixer)	
μ = dynamic viscosity of liquid	Nsec/m^2
ν = kinematic viscosity of liquid	m^2/sec
ρ = density of liquid	kg/m^3
ω = angular velocity	sec^{-1}
$\tau = \frac{TQ\text{th}}{V}$ = dimensionless mixing time	
$\frac{\rho n^2 d^2}{\Delta \rho g H}$ = density Froude number	
$\frac{\rho n d^2}{\mu}$ = Reynolds number	
$\frac{d^3}{D^{2.5} H^{0.5}}$ = dimensionless group comparing the dimensions of the stirrer and the dimensions of the mixing vessel	
$\frac{P}{\rho n^3 d^5}$ = dimensionless power consumption	

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Uni-directional heat and mass transfer at high humidities in a wetted wall column

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Summary—Further work is presented on simultaneous and adiabatic heat and mass transfer at high humidities. In previous work [1] the authors studied heat and mass transfer in opposite directions in a wetted wall tower. In the present study the authors have investigated the transfer of heat and mass in the same direction, in a similar wetted wall column.

Data were obtained for the range 0·49 to 0·80 for the mol fraction of the diffusing vapour in the gas film.

The equations of Chilton and Colburn [2] and Colburn and Drew [4] which were found to be not applicable for adiabatic humidification at high humidities, are also not applicable to the new data. The mass transfer data could not be correlated as a function of (p_{BM}/P) as before, since the effect of a, the ratio of the nett sensible heat carried by the diffusing vapour to the heat transferred in the absence of mass transfer, had to be included.

The heat transfer data for both adiabatic humidification and dehumidification were correlated by

$$(h/h_0)/\left(1+\frac{a}{2}\right) = (p_{BM}/P)^{0.22}$$

which may be written

$$(h/cG)\cdot Pr^{2/3}(p_{BM}/P)^{-0.22}/\left(1+\frac{a}{2}\right) = 0.025\,Re^{-0.2}$$

Résumé—Les auteurs présentent un nouveau travail sur le transfert simultané et adiabatique de chaleur et de masse pour des humidités élevées. L'étude se fait dans une colonne à parois mouillées comme précédemment, mais avec les transferts de masse et de chaleur s'effectuant dans le même sens au lieu de s'effectuer dans des directions opposées.

La fraction moléculaire de la vapeur diffusant dans le film gazeux correspond à l'intervalle 0,49–0,80.

Les équations de Chilton et Colburn et de Colburn et Drew qui ne s'appliquaient pas à l'humidification adiabatique pour des humidités élevées, ne s'appliquent pas d'avantage aux nouvelles déterminations. On ne peut pas, comme précédemment, représenter les valeurs du transfert de masse par une fonction de (p_{BM}/P) puis-qu'il faut tenir compte du facteur "a," rapport de la chaleur sensible, nette apportée par la vapeur diffusante à la chaleur transmise en absence du transfert de masse.

Pour une humidification et une déshumidification adiabatiques, le transfert de chaleur peut être représenté par les deux équations ci-dessous :

$$(h/h_0)/\left(1+\frac{a}{2}\right) = (p_{BM}/P)^{0.22}$$

et

$$(h/cG)\cdot Pr^{2/3}(p_{BM}/P)^{-0.22}/\left(1+\frac{a}{2}\right) = 0.025\,Re^{-0.2}$$

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Introduction

This paper is a continuation of previous work [1], in which the authors investigated the adiabatic humidification of air at high humidities in a wetted wall column. Heat and mass were transferred simultaneously in opposite directions with countercurrent flow of the liquid and gas streams. Previous correlations of Gilliland and Sherwood [5] and Chilton and Colburn [2] did not apply at high humidities.

For mol fractions of water vapour from 0·03 to 0·85 in the gas film, correlations by new heat and mass transfer factors gave :

$$j_H = (h/cG) \cdot Pr^{2/3} (p_{BM}/P)^{-0.27}$$
$$j_D = (k_G p_{BM} M_m/G) \cdot Sc^{2/3} \cdot (p_{BM}/P)^{-0.17}$$
$$= 0{\cdot}025\ Re^{-0.2} \qquad (1)$$

for a liquor rate of 77 lbs/hour in a 0·90 in. internal diameter column.

Colburn and Drew [4] theoretically developed the relation

$$q_c = h\ A\ \Delta t = \frac{a}{1 - e^{-a}} h_0\ A\ \Delta t \qquad (2)$$

to predict the effect of mass transfer on the heat transfer coefficient. h_0 is the heat transfer coefficient in the absence of simultaneous mass transfer. The dimensionless number, a, is the ratio between the nett sensible heat carried by the diffusing vapours and the heat transferred in the absence of mass transfer. This is negative if mass and heat are transferred in opposite directions and positive if mass and heat are transferred in the same directions.

The authors have previously shown that their data for heat transfer could not be correlated in the form of equation (2).

In order to test the correlations previously developed by extending the value of a to the positive region, it was decided to operate the wetted wall column so that the gas stream was simultaneously cooled and dehumidified. The theory of Colburn and Drew predicts that the heat transfer coefficient will be increased by vapour diffusing in the same direction as the heat transfer.

Experimental Procedure and Results

The original apparatus was modified slightly to permit the study of unidirectional heat and mass transfer. The make-up water system was replaced by a vessel provided with an overflow to maintain a constant amount of water in the liquid recirculation system. The water vapour condensed in the column was measured by the amount drawn off from this overflow. Apart from the measurement of the overflow in place of make up, the procedure was identical with that previously described except that the entering water temperature at the top was maintained lower than that leaving the bottom. An inherent feature of the operation of this apparatus is that for mass to be transferred to the water simultaneously with heat, the bottom and top temperatures cannot be matched.

Further modifications included the installation of a larger condenser and the 0·9 in. column previously used was replaced by a tube 1·04 in. internal diameter and 37¼ in. long. A gear pump was used on the liquid recirculation system in conjunction with a constant head feed in place of the centrifugal pump, which initially gave trouble due to leaks in this work.

A calibrated Smith dry gas meter, 0-100 c.f.h., was used to measure the volume of atmospheric air entering the column together with a rotameter for control. The water system flowrator was calibrated for temperature variations since the sensible heat gained by the water is, in this case, equal to the enthalpy change of the air stream, and the water rate is required to be known accurately.

The experimental results obtained are shown in Table 1.

Methods of Calculation

The runs were interpreted in the same manner as in the previous work. The mass transfer rate was taken as the mean between the overflow and the difference between the total water vapour entering and leaving the column. The total water vapour entering the column is the sum of the water vapour from the boiler and the incoming air

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Table 1. *Experimental results.*

Run No.	Dry air rate (lbs/hour)	H air lbs/lb dry air		Boiler rate	Condensate rate	Product rate	Overflow rate	Mixture Temp. at column °F		Column pres.	Liquor rate at top	Water temp. at column	
		In	Out	(lbs/hr)	(lbs/hr)	(lbs/hr)	(lbs/hr)	Top	Bottom	atm.	(lbs/hr)	Top	Bottom
1	4·238	·0073	·0135	5·70	·148	4·283	1·213	266	348	1·015	73·7	169·6	187·4
2	3·055	·0092	·0168	5·70	·180	4·127	1·242	262	318	1·013	73·9	174·3	192·0
3	2·203	·0098	·0137	5·70	·234	4·024	1·411	261	324	1·013	74·0	177·5	196·7
4	3·002	·0076	·0196	5·70	·175	4·975	·524	262	325	1·000	74·0	186·9	196·7
5	4·256	·0065	·0310	5·70	·150	4·564	·811	257	325	1·007	71·0	175·3	190·2
6	1·371	·0062	·0260	5·75	·191	5·104	·432	345	509	1·004	71·5	189·0	203·0
7	3·982	·0054	·0343	5·75	·095	5·297	·245	340	507	1·004	71·2	180·6	193·9
8	6·420	·0060	·0223	5·70	·040	4·689	·877	349	522	1·007	70·9	156·3	181·9
9	6·354	·0053	·0275	5·70	·038	5·018	·531	340	509	1·008	71·0	164·8	184·3
10	6·373	·0058	·0278	5·70	·086	4·491	1·058	221	261	1·007	70·8	160·8	178·7
11	6·334	·0080	·0305	5·733	·093	5·083	·418	221	256	1·007	71·0	176·6	184·5
12	3·894	·0096	·0225	5·667	·135	4·649	·716	226	265	1·005	71·1	179·5	190·9
13	1·471	·0095	·0168	5·70	·240	4·708	·734	230	257	1·004	71·3	191·1	200·6
14	1·466	·0095	·0153	5·70	·234	3·798	1·605	228	257	1·004	71·3	176·3	199·1
15	3·684	·0097	·0190	5·70	·127	4·000	1·463	230	272	1·004	71·0	163·8	186·4
16	3·311	·0096	·0182	5·70	·140	3·995	1·500	226	262	1·008	71·1	166·1	189·0

N.B. – All calculations were carried through to four significant figures to avoid cumulative errors associated with the length of the calculations.

corrected for the condensate from the steam line. The total water vapour leaving the column is the sum of the water vapour in the exit air and the water from the condensed product. The mass balances are expressed as an error in closure defined by :

$$\% \text{ error in closure} = \frac{\text{total vapour in} - \text{total vapour out}}{\text{overflow}} \times 100$$

The inlet humidity was calculated from the dry air rate and the mean of the total water vapour entering the column and the total water vapour leaving the column plus the mean mass transfer rate. The outlet humidity was calculated from the dry air rate and the mean of the total water vapour leaving the column and the difference between the total water vapour entering the column and the mean mass transfer rate.

The driving force for mass transfer was taken as the logarithmic mean between the partial pressure driving forces at the top and bottom of the column. In order to evaluate the true mean driving force it would be necessary to find the

operating line for the cooling process. Colburn [3] suggests using the equation :

$$\frac{dp_v}{dt_g} = \frac{(P - p_v)(p_v - p_c)(e^{-a} - 1) \cdot Pr^{2/3}}{p_{BM}(t_g - t_c)\, a \qquad Sc^{2/3}} \quad (3)$$

This equation was derived on the basis of the Chilton-Colburn [2] analogy and the Colburn-Drew equation (2). In adiabatic humidification at high humidites it has been shown that these relationships do not explain the data. Hence there is little reason to expect that these relationships would hold for dehumidification. As will be seen later, the results of this investigation cannot be correlated by the Chilton-Colburn equation or the Colburn-Drew equation and that a general relationship between heat and mass transfer coefficients at high humidities is not known. Hence true mean driving forces cannot be calculated. The use of the logarithmic mean driving force was based on the close equality of this mean and the true mean for both partial pressure and temperature during adiabatic humidification [1].

The calculated mass transfer data are given in Table 2.

The heat balances were calculated from a datum of 100°F. The water rate at the bottom of the column was equal to the sum of the rate

Table 2. Calculated Mass Transfer Data.

Run No.	H at column lb/lb dry air		N_A (lb moles /hour)	$(\Delta p)_{l.m.}$ (atm.)	Re	$\frac{(k_G RTd)}{D} Re^{-0.83}$	$\frac{p_{BM}}{P}$	$\left(\frac{k_G p_{BM}}{G/M_m}\right) Sc^{2/3} Re^{0.2}$	k_G	Mass balance %
	Top	Bottom								
1	1·026	1·316	·06828	·147	3345	·0177	·423	·0114	·553	+ 2
2	1·378	1·806	·07256	·158	2966	·0195	·362	·0104	·547	+ 10
3	1·843	2·489	·07901	·158	2710	·0227	·305	·0104	·596	+ 2
4	1·676	1·849	·02878	·0589	3224	·0190	·297	·0092	·583	− 2
5	1·107	1·306	·04706	·100	3457	·0175	·395	·0105	·561	+ 9
6	3·748	4·061	·02389	·108	2552	·0096	·197	·0029	·264	− 1
7	1·365	1·426	·01856	·0569	3329	·0084	·351	·0045	·284	− 1
8	·7523	·8882	·04845	·135	3774	·0114	·506	·0087	·428	− 1
9	·8162	·8975	·02872	·096	3869	·0094	·478	·0068	·357	− 5
10	·7295	·8897	·05673	·148	4194	·0126	·494	·0094	·457	− 7
11	·8828	·8986	·02817	·060	4374	·0122	·450	·0084	·461	− 1
12	1·224	1·423	·04306	·099	3479	·0165	·371	·0093	·518	+ 16
13	3·219	3·721	·04100	·118	2751	·0159	·211	·0051	·414	+ 1
14	2·615	3·729	·09073	·189	2475	·0288	·261	·0092	·572	+ 3
15	1·110	1·518	·08340	·196	3211	·0173	·421	·0108	·507	+ 5
16	1·227	1·686	·08440	·192	3104	·0184	·398	·0109	·524	+ 2

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at the top of the column and the mean mass transfer rate. The heat balances are expressed as an error in closure defined by :

$$\% \text{ error in closure} = \frac{\left(\begin{matrix}\text{sensible heat change in the water} - \\ \text{enthalpy change in the air stream}\end{matrix}\right)}{\text{enthalpy change in air stream}} \times 100$$

In calculating the convective heat transfer coefficient the heat transferred by convection was evaluated as the sum of the sensible heat lost by the dry air, the sensible heat lost by the total water vapour entering, in cooling from the inlet to the outlet temperatures, and the sensible heat lost by the mean mass transferred in cooling from the exit gas temperature to the average liquid temperature. This quantity was corrected for radiation as before and logarithmic mean temperature differences were used.

The calculated heat transfer data are shown in Table 3.

Discussion

The results were plotted by several of the methods suggested by previous investigators. The liquor rate varied only slightly and the correction to the standard liquor rate of 77 lbs/hour was negligibly small [1] (Fig. 2). Gilliland and Sherwood [5] correlated their results at low humidities by a Nusselt type equation which for a Schmidt

Table 3. Calculated heat transfer data.

Run No.	q_T *(Btu/hr)*	q_C *(Btu/hr)*	$(\Delta t)_{\text{l.m.}}$ *(°F)*	h	$\left(\frac{h}{cG}\right) Pr^{2/3} Re^{0.2}$	$\frac{h}{h_0}$	a	$\frac{h}{h_0}\Big/\left(1+\frac{a}{2}\right)$	*Heat balance %*
1	350	328	126	3·10	·0231	·924	·208	·837	− 15
2	235	216	106	2·43	·0195	·780	·237	·697	− 14
3	246	228	103	2·64	·0227	·908	·277	·797	− 13
4	227	208	99	2·50	·0192	·768	·090	·735	− 2
5	277	259	107	2·88	·0210	·840	·140	·785	− 5
6	517	451	223	2·41	·0199	·796	·080	·765	+ 6
7	628	572	227	3·00	·0208	·832	·038	·816	+ 8
8	811	757	259	3·48	·0220	·880	·125	·828	+ 8
9	759	711	242	3·50	·0218	·872	·073	·841	+ 8
10	198	183	70	3·12	·0205	·820	·152	·762	+ 5
11	155	149	57	3·12	·0199	·796	·060	·773	− 1
12	153	142	59	2·87	·0214	·856	·131	·803	− 11
13	91	79	47	2·01	·0174	·696	·145	·649	− 16
14	116	103	55	2·23	·0206	·824	·341	·704	− 5
15	187	175	76	2·74	·0214	·856	·266	·756	− 4
16	172	160	66	2·89	·0231	·924	·280	·811	− 2

number of 0·55 and a liquor rate of 77 lbs/hour may be reduced to

$$(k_G\, RTd/D)\,(p_{BM}/P) \cdot Re^{-0.83} = 0.017 \quad (4)$$

The present authors correlated their data for adiabatic humidification, for high humidities at a liquor rate of 77 lbs/hour by the Nusselt type equation

$$(k_G\, RTd/D)\,(p_{BM}/P)^{0.83} \cdot Re^{-0.83} = 0.016 \quad (5)$$

The results for dehumidification are plotted in Fig. 1 and the data are seen to fall consistently below the lines of equations (4) and (5). The data are too scattered to permit a correlation in the form of equations (4) and (5).

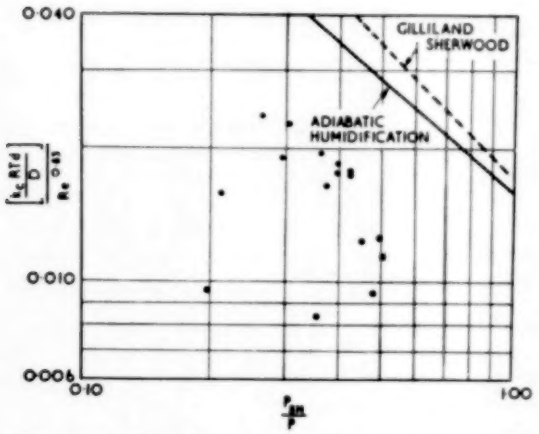

FIG. 1. Comparison of the mass transfer data with equations (4) and (5).

CHILTON and COLBURN [2] correlated the heat and mass transfer data at low humidities inside tubes by equations which at a liquor rate of 77 lbs/hour are

$$(h/cG)\, Pr^{2/3} = (k_G\, p_{BM}\, M_m/G) \cdot Sc^{2/3} = 0.026\, Re^{-0.2} \quad (6)$$

CAIRNS and ROPER [1] correlated their heat and mass transfer data by equation (1) for high humidities. The experimental mass transfer data for unidirectional transfer, as shown in Fig. 2, fall below the lines of equation (1) and (6). The points in Fig. 2 are scattered and a satisfactory correlation of the data in the form of equations

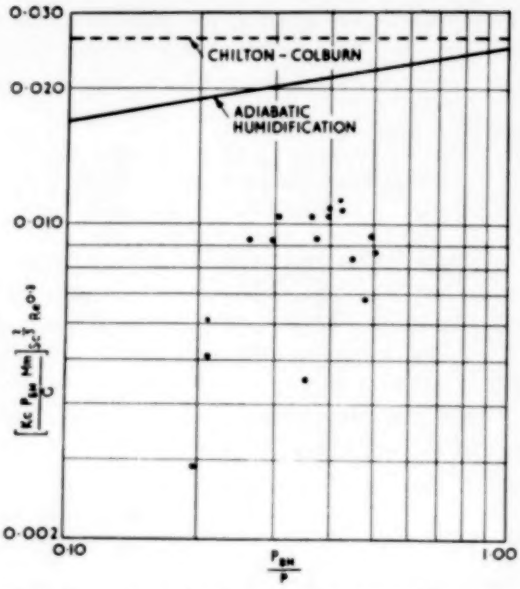

FIG. 2. Comparison of the mass transfer data with equations (1) and (6).

(1) and (6) is not possible. It was assumed that there is a relationship between

$$\log (k_G\, p_{BM}\, M_m/G) \cdot Sc^{2/3} \cdot Re^{0.2}$$

and $\log (p_{BM}/P) + ba$

where b is a constant. The data were best fitted when b was taken as 1·85. The plot of these groups is shown in Fig. 3. It was not possible to correlate the data of adiabatic humidification and dehumidification by this type of correlation. The adiabatic humidification data lie above the line shown in Fig. 3. The theoretical point shown in Fig. 3 is the point representing the CHILTON-COLBURN correlation for the case of dilute mixtures, i.e. when $(p_{BM}/P) = 1$, and $a = 0$.

The heat transfer data have been plotted in Fig. 4 in the form of (h/cG). $Pr^{2/3}\, Re^{0.2}$ versus (p_{BM}/P) as suggested by CAIRNS and ROPER. The data fall consistently below the CHILTON-COLBURN line and above the line representing the data for adiabatic humidification. No correlation was made of the data in this form but it is evident that higher coefficients are obtainable with positive values of a than for negative values, as in adiabatic humidification.

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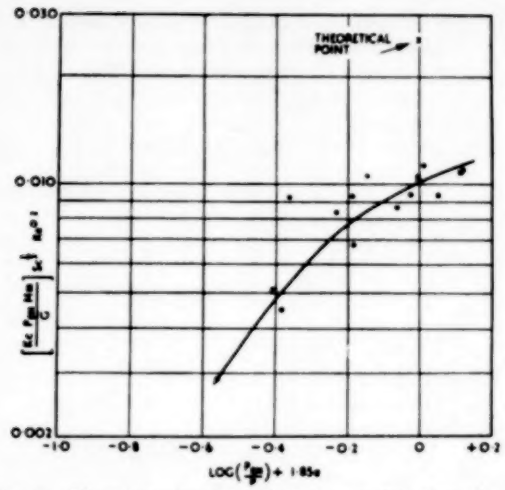

FIG. 8. Mass transfer data plotted as a function of $\log\left(\frac{p_{BM}}{p} + 1{\cdot}85a\right)$.

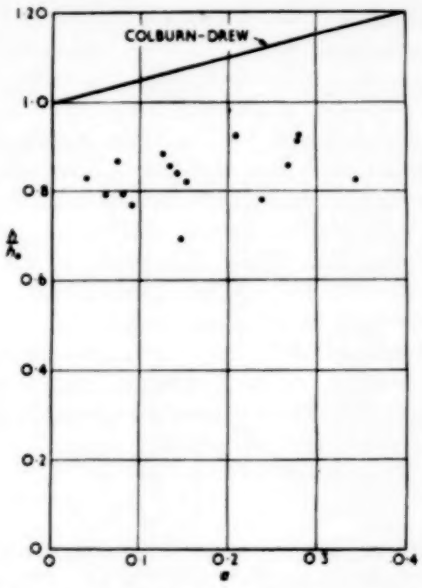

FIG. 5. Comparison of the heat transfer data with the theoretical equation (2) of COLBURN and DREW.

The ratio h/h_0 versus a is plotted in Fig. 5. As was the case for adiabatic humidification, it was not possible to correlate the data. The theoretical line of COLBURN and DREW is shown also in Fig. 5. The COLBURN and DREW equation can be re-arranged to give

$$h/h_0 = \frac{a}{1 - e^{-a}} \doteq 1 + \frac{a}{2} \qquad (7)$$

for the values of a used in this investigation. In Fig. 6 the dimensionless group $(h/h_0)/\left(1 + \frac{a}{2}\right)$ has been graphed against (p_{BM}/P) for both adiabatic humidification and dehumidification. The whole of the data can be well correlated by the equation

$$h/h_0 = \left(1 + \frac{a}{2}\right)(p_{BM}/P)^{0{\cdot}22} \qquad (8)$$

which can be written

$$(h/cG) \cdot Pr^{2/3} \cdot (p_{BM}/P)^{-0{\cdot}22} / \left(1 + \frac{a}{2}\right) = 0{\cdot}025\, Re^{-0{\cdot}2} \qquad (9)$$

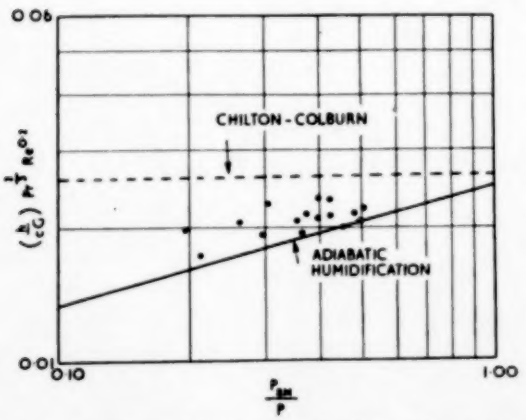

FIG. 4. Comparison of the heat transfer data with equations (1) and (6).

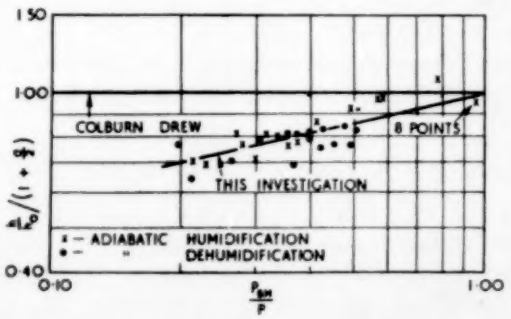

FIG. 6. Comparison of the heat transfer data for both adiabatic humidification and dehumidification with (p_{BM}/P).

CONCLUSION

Mass transfer coefficients for the case of adiabatic dehumidification can be correlated by inclusion of the groups (p_{BM}/P) and a and are not a function of (p_{BM}/P) alone as was the case for adiabatic humidification. The presence of heat transfer appears to have reduced the mass transfer rate.

The presence of mass transfer, when occurring in the same direction as heat transfer, increases the heat transfer rate, as was predicted by COLBURN and DREW. These increased heat transfer coefficients can be correlated only by inclusion of both groups (p_{BM}/P) and a, and are not a function of a alone as was derived by COLBURN and DREW. The correlation is made for both humidification and dehumidification.

NOTATION

a = the ratio between the nett sensible heat carried by the diffusing vapours and the heat transferred in the absence of mass transfer.
A = the area of the gas-liquid interface, taken as the inside area of the column, when dry, sq. ft.
b = a constant.
c = specific heat, Btu/(lb.)(°F).
d = diameter of column, ft.
D = molecular diffusivity of the diffusing component sq. ft./hr.
e = base of Naperian logarithms.
G = mass velocity, lb./(hr.) (ft.^{2}).
h = convective heat transfer coefficient, Btu/(hr.) (ft.^{2}) (°F.).
h_0 = convective heat transfer coefficient in the absence of mass transfer, Btu/(hr.) (ft.^{2}) (°F).
H = humidity, lb. of water vapour per lb. of dry air
j_D = mass transfer factor $= (k_G\, p_{BM}\, M_m/G)\, Sc^{2/3}\, (P_{BM}/P)^{-0.17}$
j_H = heat transfer factor $= (h/cG)\, Pr^{2/3} (p_{BM}/P)^{-0.27}$
k = thermal conductivity, Btu/(hr.) (ft.) (°F).
k_G = the gas film coefficient of mass transfer, lb. moles/(hr.) (ft.^{2}) (atm.)
M_m = the molecular weight of the gas-vapour mixture in the main stream
N_A = the rate of evaporation of water vapour, lb. moles/hr.
P = total pressure, atm.
P_{BM} = the logarithmic mean partial pressure of the non-diffusing gas in the gas film, atm.
p_c = vapour pressure at t_c, atm.
p_v = partial pressure of the vapour in the main stream, atm.
$(\Delta p)_{l.m.}$ = the logarithmic mean between the driving forces at each end of the column, atm.
Pr = Prandtl number $= c\mu/k$.
q_C = the rate of heat transfer by convection, Btu/hr.
q_T = the total rate of heat transfer, Btu/hr.
R = gas constant, (ft.^{3}) (atm.)/(lb. mole) (°R).
R' = Reynolds number $= dG/\mu$.
Sc = Schmidt number $= \mu/\rho D$.
St = Stanton number $= h/cG$.
T = absolute temperature, °R.
t_c = temperature of the condensing surface, °F.
t_g = bulk temperature at the gas-vapour mixture, °F
Δt = temperature difference, °F.
$(\Delta t)_{l.m.}$ = logarithmic mean temperature, difference, °F.
μ = viscosity, lb./(hr.)(ft.)
ρ = density, lb./ft.^{3}

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The solution of multicomponent distillation columns

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Summary—The equations of A. J. V. UNDERWOOD for solution of distillation columns are arranged to give a solution in the form of a sum of difference products. For many distillation problems the present solution is much less tedious than the straightforward solution of UNDERWOOD's equations or the determinantal solution proposed by ALDER and HANSON [1]. The solution is illustrated by an example employing a five-component system.

Résumé—Pour la solution des équations de A. J. V. UNDERWOOD permettant le calcul des colonnes à distiller, les auteurs conseillent l'emploi d'une somme de produits d'une différence. Dans de nombreux problèmes de distillation, cette solution est beaucoup moins pénible que la solution directe des équations d'UNDERWOOD ou que la solution sous forme de déterminants proposée par ALDER et HANSON.

La solution est illustrée par un exemple sur un système à cinq composants.

THE solution of multicomponent distillation problems is, in general, time-consuming and tedious work. The methods which are available for such solutions employ various basic assumptions and various techniques, and the particular method which is best suited to the problem at hand depends largely on the accuracy of the answer desired and on the physical make-up of the system to be distilled. As an example, plate-by-plate calculation procedures are distinctly useful for some systems, for example systems in which all of the components of the feed appear in one or the other of the products in well-definable amounts and in which the difference in volatility between the key components is large. For such systems, calculation plate-by-plate from one end of the column will provide the solution within a few plates. If, on the other hand, the key components lie intermediate in volatility within a large number of components, and a large number of plates is to be expected, plate-by-plate calculations become difficult, and procedures which allow the calculation of the number of rectifying and stripping plates as complete sections become most useful. Such "group" procedures have only recently been developed, and to the authors' knowledge, four basic solutions presently exist. The relative merits of these are as yet undetermined but one which shows promise of considerable usefulness is the set of equations derived by A. J. V. UNDERWOOD [3, 4, 5].

The equations provide exact solutions of distillation columns under the basic assumptions of constant relative volatilities and constant sectional flows. The correctness of these assumptions depends upon the system, and although they are not in general exact, distillation equations involving their use have found wide application. The flows are usually set by the internal reflux at the top of the column and the thermal condition of the feed. Various procedures are in use for estimating average relative volatilities. Experience has shown that satisfactory values may be obtained using an average of the top plate and reboiler temperatures weighted by the molar amounts of top and bottom products or, alternatively, that temperature at which the product of the equilibrium constants of the light and heavy key is equal to unity.

The solution of UNDERWOOD's equations gives directly the number of rectifying and stripping

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plates. The systems ordinarily encountered in multicomponent distillation contain components both lighter than the light key and heavier than the heavy key. The trial and error solution following the lines proposed by UNDERWOOD [5] then becomes prohibitively time consuming.

ALDER and HANSON [1] have proposed a solution of the equations in determinantal form, bypassing the calculation of feed plate concentrations proposed by UNDERWOOD. However, since the order of the determinants which must be solved in the method of ALDER and HANSON is equal to the number of components in the feed, the difficulty of the solution mounts rapidly with an increase in the number of components, and a solution which would avoid this difficulty is considerably more useful. The present paper proposes a solution which accomplishes this by developing the determinants into a sum of terms, each of which contains a quotient of products of differences.

For the convenience of the reader, and to introduce the notation to be used, a brief review of the developments which led to the solution is presented. To avoid excessive duplication of previously published material, the review and the development of the solution will be presented for a specific case. The use of the solution in solving other cases can be obtained from a brief study of the previous paper by ALDER and HANSON.

For a system of three components A, B and C, then, the following equations may be written :

$$V = \frac{\alpha_A d\,(x_A)_d}{\alpha_A - \phi} + \frac{\alpha_B d\,(x_B)_d}{\alpha_B - \phi} + \frac{\alpha_C d\,(x_C)_d}{\alpha_C - \phi} \qquad (1)$$

and

$$-V' = \frac{\alpha_A b\,(x_A)_b}{\alpha_A - \phi'} + \frac{\alpha_B b\,(x_B)_b}{\alpha_B - \phi'} + \frac{\alpha_C b\,(x_C)_b}{\alpha_C - \phi'} \qquad (2)$$

where V = rectifying section vapour flow, moles

V' = stripping section vapour flow, moles

$d\,(x_i)_d$ = amount of any component i in the top product, moles

$b\,(x_i)_b$ = amount of any component i in the bottom product, moles

α_i = relative volatility of component i. All relative volatilities to be based on the same component.

ϕ = a rectifying section parameter

ϕ' = a stripping section parameter

UNDERWOOD employs equations (1) and (2) to define the rectifying and stripping section parameters, ϕ and ϕ'. It is apparent that for this three component system there are three values of ϕ which will satisfy eq. (1) such that if these are numbered in decreasing order of magnitude :

$$\alpha_A > \phi_1 > \alpha_B$$
$$\alpha_B > \phi_2 > \alpha_C$$
$$\alpha_C > \phi_3$$

There are also three values of ϕ' which will satisfy equation (2) and if these are again listed in decreasing order of magnitude :

$$\phi'_1 > \alpha_A$$
$$\alpha_A > \phi'_2 > \alpha_B$$
$$\alpha_B > \phi'_3 > \alpha_C$$

UNDERWOOD has shown that two independent equations may be written relating the three values of ϕ, the concentrations of A, B and C in the liquid on the feed plate, and the number of rectifying plates. These equations are :

$$\frac{\dfrac{\alpha_A (x_A)_f}{\alpha_A - \phi_1} + \dfrac{\alpha_B (x_B)_f}{\alpha_B - \phi_1} + \dfrac{\alpha_C (x_C)_f}{\alpha_C - \phi_1}}{\dfrac{\alpha_A (x_A)_f}{\alpha_A - \phi_2} + \dfrac{\alpha_B (x_B)_f}{\alpha_B - \phi_2} + \dfrac{\alpha_C (x_C)_f}{\alpha_C - \phi_2}} = \left(\frac{\phi_2}{\phi_1}\right)^n \qquad (3)$$

and

$$\frac{\dfrac{\alpha_A (x_A)_f}{\alpha_A - \phi_2} + \dfrac{\alpha_B (x_B)_f}{\alpha_B - \phi_2} + \dfrac{\alpha_C (x_C)_f}{\alpha_C - \phi_2}}{\dfrac{\alpha_A (x_A)_f}{\alpha_A - \phi_3} + \dfrac{\alpha_B (x_B)_f}{\alpha_B - \phi_3} + \dfrac{\alpha_C (x_C)_f}{\alpha_C - \phi_3}} = \left(\frac{\phi_2}{\phi_3}\right)^n \qquad (3')$$

where $(x_i)_f$ = mole fraction of component i in the liquid on the feed plate.

n = rectifying plates, including the feed plate.

The authors, to simplify the writing of such equations have adopted a shorter nomenclature, where

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$$\frac{\alpha_A}{\alpha_A - \phi_1} = A_1, \frac{\alpha_B}{\alpha_B - \phi_1} = B_1, \text{ etc.}$$

and

$$\left(\frac{\phi_2}{\phi_1}\right)^n = \psi_{21}$$

Rewriting equations (3) and (3′), these then become

$$\frac{A_1(x_A)_f + B_1(x_B)_f + C_1(x_C)_f}{A_2(x_A)_f + B_2(x_B)_f + C_2(x_C)_f} = \psi_{21} \qquad (3)$$

and

$$\frac{A_2(x_A)_f + B_2(x_B)_f + C_2(x_C)_f}{A_3(x_A)_f + B_3(x_B)_f + C_3(x_C)_f} = \psi_{32} \qquad (3')$$

Similarly, two independent equations can be written for the stripping section :

$$\frac{A_2'(x_A)_f + B_2'(x_B)_f + C_2'(x_C)_f}{A_1'(x_A)_f + B_1'(x_B)_f + C_1'(x_C)_f} = \psi_{21}' \qquad (4)$$

$$\frac{A_3'(x_A)_f + B_3'(x_B)_f + C_3'(x_C)_f}{A_2'(x_A)_f + B_2'(x_B)_f + C_2'(x_C)_f} = \psi_{32}' \qquad (4')$$

where :

$$A_2' = \frac{\alpha_A}{\alpha_A - \phi_2'}, \quad B_2' = \frac{\alpha_B}{\alpha_B - \phi_2'}, \text{ etc.}$$

and

$$\psi_{21}' = \left(\frac{\phi_2'}{\phi_1'}\right)^m$$

where m = stripping plates, including the reboiler but not the feed plate.

If components B and C are the key components and their separation is set, then the amounts of these components in the top and bottom products are known. As an approximation for the first solution, it will be assumed that component A goes completely into the top product. This approximation may be corrected to any desired degree of accuracy later and does not represent a loss in accuracy of the calculation. If, then, the reflux is set, the quantities V and V' are known and the ϕ and ϕ' values may be calculated from equations (1) and (2). It will be noted that a consequence of the approximation of no component A in the bottom product is that $\phi_1' = \alpha_A$. This means that A_1' or $\alpha_A/(\alpha_A - \phi_1')$ is equal to infinity and as a result eq. (4) becomes useless. Equations (3), (3′), and (4′) can be written out however and solved for n and m.

Alder and Hanson have suggested that the solution of these equations be accomplished by solution of the third order determinant which can be set up as follows :

$$\begin{vmatrix} A_1 - A_2\psi_{21} & B_1 - B_2\psi_{21} & C_1 - C_2\psi_{21} \\ A_2 - A_3\psi_{32} & B_2 - B_3\psi_{32} & C_2 - C_3\psi_{32} \\ A_3' - A_2'\psi_{32}' & B_3' - B_2'\psi_{32}' & C_3' - C_2'\psi_{32}' \end{vmatrix} = 0 \quad (5)$$

The unknowns n and m are contained as exponents in the ψ and ψ' terms. If a value of n is set, the corresponding value of m may be calculated from eq. (5), and in this way the picture of all possible combinations of rectifying and stripping plates which will perform the distillation can be found.

The solution of eq. (5) is not difficult. However, if, for example, a five component system were to be distilled, eq. (5) would become a fifth order determinant and the solution would be considerably more tedious. Since the number of components in the feed is equal to the order of the determinant to be solved, as the number of components increases, the labour of solution becomes prohibitive. However, by further development, the solution can be reduced from determinantal form to a difference product form which is much easier to solve.

Eq. (5) may be written :

$$\begin{vmatrix} A_1\psi_1 - A_2\psi_2 & B_1\psi_1 - B_2\psi_2 & C_1\psi_1 - C_2\psi_2 \\ A_2\psi_2 - A_3\psi_3 & B_2\psi_2 - B_3\psi_3 & C_2\psi_2 - C_3\psi_3 \\ A_3'\psi_3' - A_2'\psi_2' & B_3'\psi_3' - B_2'\psi_2' & C_3'\psi_3' - C_2'\psi_2' \end{vmatrix} = 0 \quad [(6)$$

where

$$\psi_1 = \phi_1^n, \ \psi_2 = \phi_2^n, \text{ etc.}$$

$$\psi_3' = (1/\phi_3')^m, \ \psi_2' = (1/\phi_2')^m, \text{ etc.}$$

It is apparent that the term $\alpha_A \alpha_B \alpha_C$ can be cancelled out of the determinant, eq. (6). The term $A_1\psi_1$, for example, is then $\dfrac{1}{\alpha_A - \phi_1}\psi_1$.

Rewriting eq. (6) in a new nomenclature to show the dropping of all α values in the numerators of the individual terms is not worthwhile, however, and it can merely be understood that for the rest of the development, $A_1 = \dfrac{1}{\alpha_A - \phi_1}$,

etc. This lapse in preciseness of nomenclature here leaves no ambiguity in the final solution.

Eq. (6) can also be factored into six third order determinants to give :

$$\psi_1\,\psi_2\,\psi_3' \begin{vmatrix} A_1 & A_2 & A_3' \\ B_1 & B_2 & B_3' \\ C_1 & C_2 & C_3' \end{vmatrix} - \psi_1\,\psi_2\,\psi_2' \begin{vmatrix} A_1 & A_2 & A_2' \\ B_1 & B_2 & B_2' \\ C_1 & C_2 & C_2' \end{vmatrix}$$

$$- \psi_1\,\psi_3\,\psi_3' \begin{vmatrix} A_1 & A_3 & A_3' \\ B_1 & B_3 & B_3' \\ C_1 & C_3 & C_3' \end{vmatrix} + \ldots . = 0 \qquad (7)$$

If the first determinant in eq. (7) is written out, it is :

$$\begin{vmatrix} \frac{1}{\alpha_A - \phi_1} & \frac{1}{\alpha_A - \phi_2} & \frac{1}{\alpha_A - \phi_3'} \\ \frac{1}{\alpha_B - \phi_1} & \frac{1}{\alpha_B - \phi_2} & \frac{1}{\alpha_B - \phi_3'} \\ \frac{1}{\alpha_C - \phi_1} & \frac{1}{\alpha_C - \phi_2} & \frac{1}{\alpha_C - \phi_3'} \end{vmatrix}$$

Such a determinant is a double alternant and can also be written [2] as

$$\frac{(-1)^{\frac{(k)\,(k-1)}{2}}\,\zeta^{\frac{1}{2}}(\alpha_A\,\alpha_B\,\alpha_C)\,\zeta^{\frac{1}{2}}(\phi_1\,\phi_2\,\phi_3')}{u_A\,u_B\,u_C}$$

where k = the order of the determinant.

$\zeta^{\frac{1}{2}}$ = difference product obtained by taking each term and subtracting from it in turn each term preceding, then multiplying all of these differences together.

u_A = difference product obtained by multiplying together all terms $(\alpha_A - \phi_r)$ where ϕ_r is a general value of ϕ which will take all values of ϕ used in the determinant.

u_B = a difference product exactly like u_A except that α_B is used in place of α_A. etc.

Before proceeding, some simplification can be effected. Two factors enter into each determinant in eq. (7) and may be cancelled. Thus we may drop the terms

$$(-1)^{\frac{(k)\,(k-1)}{2}}$$

and

$$\zeta^{\frac{1}{2}}(\alpha_A\,\alpha_B\,\alpha_C)$$

If these factors are dropped, then the first term in equation (7) becomes :

$$\frac{(\psi_1\,\psi_2\,\psi_3')\;\zeta^{\frac{1}{2}}(\phi_1\,\phi_2\,\phi_3')}{u_A\,u_B\,u_C}$$

and if this is written out it is :

$$\frac{(\psi_1\,\psi_2\,\psi_3')\,[(\phi_1-\phi_2)\,(\phi_1-\phi_3')\,(\phi_2-\phi_3')]}{[(\alpha_A-\phi_1)\,(\alpha_A-\phi_2)\,(\alpha_A-\phi_3')]} \times$$

$$\frac{1}{[(\alpha_B-\phi_1)\,(\alpha_B-\phi_2)\,(\alpha\ \ -\phi_3')]} \times$$

$$\frac{1}{[(\alpha_C-\phi_1)\,(\alpha_C-\phi_2)\,(\alpha_C-\phi_3')]}$$

It will be noted that the liberty of writing the difference product, $\zeta^{\frac{1}{2}}(\phi_1\,\phi_2\,\phi_3')$ with all terms reversed has been taken. It is more natural to calculate the difference product this way, subtracting ϕ and ϕ' values from ϕ or ϕ' values preceding, and it yields the same results in the summation of terms in eq. (7).

For illustration, the second term in eq. (7) is

$$\frac{-(\psi_1\,\psi_2\,\psi_2')\,\zeta^{\frac{1}{2}}(\phi_1\,\phi_2\,\phi_2')}{u_A\,u_B\,u_C}$$

or written out

$$\frac{-(\psi_1\,\psi_2\,\psi_2)\,[(\phi_1-\phi_2)\,(\phi_1-\phi_2')\,(\phi_2-\phi_2')]}{[(\alpha_A-\phi_1)\,(\alpha_A-\phi_2)\,(\alpha_A-\phi_2')]} \times$$

$$\frac{1}{[(\alpha_B-\phi_1)\,(\alpha_B-\phi_2)\,(\alpha_B-\phi_2')]} \times$$

$$\frac{1}{[(\alpha_C-\phi_1)\,(\alpha_C-\phi_2)\,(\alpha_C-\phi_2')]}$$

The other terms in eq. (7) are constructed in the same way.

At first acquaintance, the terms in the difference product solution of eq. (7) seem quite long and involved, and in the extension of the method to systems of several components, it appears at first that even the work of keeping track of the major terms in equations of the type of eq. (7) will be difficult. Since this is one of the chief

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difficulties in the difference product solution, it is very important to set up a standard procedure and a set of rules that will make the difference product solution as automatic as possible. For this purpose, the general form of equation (7) may be written as:

$$\left.\begin{aligned}&\Sigma \frac{(-1)^{(o+p+q+\ldots r+s+t+\ldots)}}{u_o\, u_p\, u_q \ldots u'_r\, u'_s\, u'_t \ldots}\\ &\frac{(\psi_o\, \psi_p\, \psi_q \ldots \psi'_r\, \psi'_s\, \psi'_t \ldots)}{u_o\, u_p\, u_q \ldots u'_r\, u'_s\, u'_t \ldots}\\ &\frac{\zeta^{\frac{1}{2}}(\phi_o\, \phi_p\, \phi_q \ldots \phi'_r\, \phi'_s\, \phi'_t)}{u_o\, u_p\, u_q \ldots u'_r\, u'_s\, u'_t \ldots}\end{aligned}\right\} = 0 \qquad (7)$$

In general this equation is the solution of a determinant of the type of eq. (6). The order of the determinant is equal to the number of components in the feed, and in a case where the separation of the two key components has been set and the reflux has been set, one such determinant can be written [1]. This determinant will in general employ all of the ϕ values which are useful and all of the ϕ' values which are useful, thus excluding ϕ and ϕ' values which are equal to relative volatilities. The total number of useful ϕ and ϕ' values will equal the number of components plus two: the number of ϕ values and the number of ϕ' values will vary depending on where the key components lie in the list of components.

The rules which may then be set up for the solution of equation (7) are as follows:

1. Each major term in the summation will be characterized by one less than the number of useful ϕ values and one less than the number of useful ϕ' values. Thus the number of ψ values written down in each term is one less than the number of useful ϕ values, and the number of ψ' values written down in each term is one less than the number of useful ϕ' values.

2. The total number of ψ and ψ' values written down in each term is equal to the number of components.

3. The ψ values are written down in ascending order of magnitude of subscripts (descending order of magnitude of ϕ). The ψ' values are written down in ascending order of magnitude of subscripts (descending order of magnitude of ϕ').

4. All of the ψ values are written down first, followed by the ψ' values.

5. The combinations of ψ and ψ' values used are all possible combinations under rules (1), (2), (3) and (4) which do not contain any repeating ψ or ψ' values. Thus, the number of combinations possible and also the number of major terms in the summation is equal to the number of useful ϕ values times the number of useful ϕ' values.

6. The difference product $\zeta^{\frac{1}{2}}(\phi_o\, \phi_p\, \phi_q \ldots \ldots \phi'_r\, \phi'_s\, \phi'_t \ldots .)$ is obtained by subtracting each ϕ or ϕ' value from all ϕ or ϕ' values preceding it in the order of listing of the ψ and ψ' values and multiplying these differences together. Thus $\zeta^{\frac{1}{2}}(\phi_o\, \phi_p\, \phi_q \ldots \ldots \phi'_r\, \phi'_s\, \phi'_t \ldots .) = [(\phi_o - \phi_p)(\phi_o - \phi_q) \ldots (\phi_o - \phi'_r)(\phi_o - \phi'_s)(\phi_o - \phi'_t) \ldots] [(\phi_p - \phi_q) \ldots . (\phi_p - \phi'_r)(\phi_p - \phi'_s)(\phi_p - \phi'_t) \ldots] [(\phi_q - \phi'_r)(\phi_q - \phi'_s)(\phi_q - \phi'_t) \ldots] \ldots . [(\phi'_r - \phi'_s)(\phi'_r - \phi'_t) \ldots .] [(\phi'_s - \phi'_t) \ldots .] \ldots \ldots$

7. The number of u values in each term is equal to the number of ϕ and ϕ' values used in the term. For convenience these have been grouped and characterized by a ϕ or ϕ' value rather than by component. Thus $u_1 = (\alpha_A - \phi_1)(\alpha_B - \phi_1)(\alpha_C - \phi_1)(\alpha_D - \phi_1) \ldots \ldots \ldots$, $u'_2 = (\alpha_A - \phi'_2)(\alpha_B - \phi'_2)(\alpha_C - \phi'_2)(\alpha_D - \phi'_2) \ldots .$ etc.

8. Each term in the summation is multiplied by -1 or $+1$ depending on the sum of the subscripts of all ϕ and ϕ' values used in the term. Since the choice is arbitrary, the convention has been adopted that if the sum of the subscripts is even, the term is multiplied by $+1$ and if the sum of the subscripts is odd, the term is multiplied by -1.

The rules set down here completely define

the solution of the determinant and enable calculation of the column. Some study of them is necessary, however, before much facility in such solutions is gained, and to aid in this understanding of the method an example of a distillation column separating a five component system has been solved for presentation here.

Consider a five component system of *A*, *B*, *C*, *D*, *E*. The feed to the column is saturated liquid of the composition shown in the table below, and the relative volatilities based on the heavy key, *D*, are as shown :

	X_F	α
A	0·05	5
B	0·25	2·5
C	0·40	2·2
D	0·20	1·0
E	0·10	0·6

Components *C* and *D* are the key components. Specifications on their separation are set so that 95% of *C* goes into the top product and 90% of *D* goes into the bottom product. It is assumed as a first approximation that the light diluents, *A* and *B*, go completely into the top product and that the heavy diluent, *E*, goes completely into the bottom product. Thus the products, based on one mole of feed, are :

	$d\,(x_i)_d$	$b\,(x_i)_b$
A	0·05	—
B	0·25	—
C	0·38	0·02
D	0·02	0·18
E	—	0·10

The minimum rectifying section vapour flow for this separation is calculated to be 1·206 moles/mole of feed. An operating rectifying section vapour flow of 1·6 moles/mole of feed, or approximately 130% of minimum, was chosen for the calculation.

With these variables set, there is an infinite number of rectifying and stripping plate combinations which will perform the distillation, and the answer desired is the combination of rectifying plates and stripping plates which will constitute a minimum of total plates, or will give the optimum feed plate location. Generally the minimum in the curve of total plates verses feed plate location is very flat, and a wide choice of feed plate location can be made with little effect on the total plate requirements.

The first step in solution of the problem is the calculation of the ϕ and ϕ' values. This calculation is the solution of the following equations :

For values of ϕ :

$$1{\cdot}6 = \frac{5\,(0{\cdot}05)}{5-\phi} + \frac{2{\cdot}5\,(0{\cdot}25)}{2{\cdot}5-\phi} + \frac{2{\cdot}2\,(0{\cdot}38)}{2{\cdot}2-\phi} + \frac{1\,(0{\cdot}02)}{1-\phi} \quad (8)$$

For values of ϕ' :

$$-1{\cdot}6 = \frac{2{\cdot}2\,(0{\cdot}02)}{2{\cdot}2-\phi'} + \frac{1\,(0{\cdot}18)}{1-\phi'} + \frac{0{\cdot}6\,(0{\cdot}10)}{0{\cdot}6-\phi'} \quad (9)$$

Equations (8) and (9) may be solved by any of the iteration methods available for solution of cubic and higher order equations. Actually, trial-and-error solution is quite rapid and has the advantage that in the solution for ϕ or ϕ', the quantities $\alpha_A - \phi_1$, etc., are calculated. Since these differences are of use later it is convenient to have them tabulated as a result of this first calculation.

Solving eq. (8), then, the following values of ϕ are found :

$$\phi_1 = 4{\cdot}885$$
$$\phi_2 = 2{\cdot}393$$
$$\phi_3 = 1{\cdot}382$$
$$\phi_4 = 0{\cdot}9566$$
$$\phi_5 = 0{\cdot}6$$

It will be noted that a value of ϕ_5 is listed. If the assumption is made that $d\,(x_E)_d = 0$, then $\phi_5 = \alpha_E$ and may be listed as such although it is of no use in solving the column.

Similarly, from eq. (9) the following values of ϕ' are found :

$$\phi_1' = 5$$
$$\phi_2' = 2{\cdot}5$$
$$\phi_3' = 2{\cdot}2311$$
$$\phi_4' = 1{\cdot}118$$
$$\phi_5' = 0{\cdot}6284$$

Here again values are listed for ϕ_1' and ϕ_2'. Under the assumptions of $b\,(x_A)_b = 0$ and $b\,(x_B)_b = 0$, the values of ϕ_1' and ϕ_2' are respectively equal to α_A and α_B. These values of ϕ_1' and ϕ_2' are of no

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use in solving the column, but are listed in order to clarify the system for subscript numbering of the ϕ' values.

Three significant figures are being carried in the calculations at this point, although it is apparent that this necessitates having more than three significant figures in the ϕ and ϕ' values.

The ϕ values to be used in the solution are ϕ_1, ϕ_2, ϕ_3, and ϕ_4. The ϕ' values to be used are ϕ'_3, ϕ'_4, and ϕ'_5. Generally, the next step in calculation is to form a table listing the characterizing ψ and ψ' combinations. In the table may be listed, then, the other terms which accompany the characterizing ψ and ψ' combination in equation (7). These are: in the numerator, the term $(-1)^{(o+p+q+\ldots r'+s'+t'+\ldots)}$, which will be called simply the sign; in the numerator the value of the difference product, $\zeta^{\frac{1}{2}}(\phi \ldots\ldots)$; and in the denominator the term $u_o u_p \ldots$ Such a table has been constructed for the example and is shown in Table 1. In the first column are listed all of the characterizing ψ and ψ' combinations which are possible under the rules. As an illustration, the various items in the first row of the table will be calculated out here:

The sign by which the term is to be multiplied is determined by $(-1)^{(\Sigma \text{ subscripts on } \psi \text{ and } \psi' \text{ values})}$ which, for the first combination, is $(-1)^{(1+2+3+4+5)} = (-1)^{15} = -1$. The sign is thus minus.

Next the difference product is, when written out:

$$\begin{aligned}\zeta^{\frac{1}{2}}(\phi \ldots\ldots) &= [(\phi_1 - \phi_2)\ (\phi_1 - \phi_3)\ (\phi_1 - \phi'_4)\ (\phi_1 - \phi'_5)]\ [(\phi_2 - \phi_3)\ (\phi_2 - \phi'_4)\ (\phi_2 - \phi'_5)]\ [(\phi_3 - \phi'_4)\ (\phi_3 - \phi'_5)]\ [(\phi'_4 - \phi'_5)] \\ &= [(2{\cdot}49)\ (3{\cdot}50)\ (3{\cdot}77)\ (4{\cdot}26)]\ [(1{\cdot}01)\ (1{\cdot}28)\ (1{\cdot}77)]\ [(\cdot 264)\ (\cdot 754)]\ [(\cdot 490)] \\ &= +31{\cdot}0\end{aligned}$$

Lastly the product of u values $= u_1 u_2 u_3 u'_4 u'_5$ where

$$\begin{aligned}u_1 &= (\alpha_A - \phi_1)\ (\alpha_B - \phi_1)\ (\alpha_C - \phi_1)\ (\alpha_D - \phi_1)\ (\alpha_E - \phi_1) \\ &= 12{\cdot}3 \text{ etc.}\end{aligned}$$

Then $u_1 u_2 u_3 u'_4 u'_5 = +\cdot 0787$.

The various values of $\alpha - \phi_1$ are available from the calculation of ϕ_1 and it is convenient following calculation of the ϕ and ϕ' values to calculate all values of u and tabulate them for use.

These terms are entered in the table, and the rest of the table is calculated, whereupon eq. (7) may be written:

$$\begin{aligned}&-\psi_1\psi_2\psi_3\psi'_4\psi'_5\left(\frac{31{\cdot}0}{0{\cdot}0787}\right) \\ &+\psi_1\psi_2\psi_3\psi'_3\psi'_5\left(\frac{-29{\cdot}2}{-0{\cdot}0103}\right) \\ &-\psi_1\psi_2\psi_3\psi'_3\psi'_4\left(\frac{-4{\cdot}54}{0{\cdot}0269}\right) \\ &+\psi_1\psi_2\psi_4\psi'_4\psi'_5\left(\frac{-13{\cdot}2}{-0{\cdot}00956}\right) - \ldots\ldots\ldots \quad (7)\end{aligned}$$

If, now, a value of n, the number of rectifying plates, is set, from eq. (7) the corresponding value of m may be calculated. In this example the following values have been calculated:

n	m	$n+m$
6	4·5	10·5
5	5·2	10·2
4·5	6·0	10·5

It is apparent that the minimum in the curve of total plates is flat, and that $n = 5$ and $m = 5{\cdot}2$ essentially represents the optimum point.

The assumption, made at the beginning of the example, that components *A* and *B*, which are lighter than the light key, go completely into the top product, and that component *E*, heavier than the heavy key, goes completely into the bottom product, should be checked. The actual amounts of these components in the products will vary to some extent with the number of rectifying and stripping plates. Since the minimum point in total plates is of most interest, the amounts of the diluents in the products should be calculated at this point, i.e., with rectifying plates equal to 5 and stripping plates equal to 5·2. The calculation of the amount of each diluent in the products requires the solution of one additional determinant. This is identical to the solution for plates, except that the ϕ

and ϕ' values used are different. The correct values of ϕ and ϕ' to be used for the checking of each diluent is discussed in the previous paper by ALDER and HANSON [1]. Following the calculation of the amounts of the diluents in the products, the question of whether or not the calculation for the number of plates should be repeated with more correct ϕ and ϕ' values is a matter of judgment and depends on the accuracy desired in the final answer.

The calculation of this example, while it may appear so at first glance, was not excessively time consuming. Actually the most labour in such a calculation occurs in calculation of the ϕ and ϕ' values. Familiarity with the rest of the calculations leads to many short cuts which save considerable time. For example, it should be apparent that if eq. (7) is multiplied through by the product of all u values, there remain in each major term only two u values in the numerator, the values of u corresponding to the one ϕ value and the one ϕ' value which do not appear in the characterizing ψ term. Along with this simplification, others can be effected, and convenient tables can be set up for calculating the difference product terms. The amount of time which will be spent on the calculation of a column by this method is a definite function of the amount of experience with the method which the calculator possesses. Whether the method is efficient in comparison with plate-by-plate procedure is mostly dependent on the system to be fractionated, and again it must be left to the judgment of the calculator to determine whether it is desirable to employ this method. Certainly there are many cases where it will prove of considerable value.

Table I. Sample calculation

Characterizing term	*Sign*	$\zeta^{\frac{1}{2}}(\phi \ldots .)$	$u_a\, u_p \ldots .$
$\psi_1\ \psi_2\ \psi_3\ \psi_4'\ \psi_5'$	−	+ 31·0	+ 0·0787
$\psi_1\ \psi_2\ \psi_3\ \psi_3'\ \psi_5'$	+	− 29·2	− 0·0103
$\psi_1\ \psi_2\ \psi_3\ \psi_3'\ \psi_4'$	−	− 4·54	+ 0·0269
$\psi_1\ \psi_2\ \psi_4\ \psi_4'\ \psi_5'$	+	− 13·2	− 0·00956
$\psi_1\ \psi_2\ \psi_4\ \psi_3'\ \psi_5'$	−	− 30·4	+ 0·00125
$\psi_1\ \psi_2\ \psi_4\ \psi_3'\ \psi_4'$	+	+ 6·64	− 0·00328
$\psi_1\ \psi_3\ \psi_4\ \psi_4'\ \psi_5'$	−	− 0·484	− 0·0705
$\psi_1\ \psi_3\ \psi_4\ \psi_3'\ \psi_5'$	+	+ 28·4	+ 0·00922
$\psi_1\ \psi_3\ \psi_4\ \psi_3'\ \psi_4'$	−	− 3·00	− 0·0241
$\psi_2\ \psi_3\ \psi_4\ \psi_4'\ \psi_5'$	+	− 0·00717	− 0·000767
$\psi_2\ \psi_3\ \psi_4\ \psi_3'\ \psi_5'$	−	+ 0·0758	+ 0·000101
$\psi_2\ \psi_3\ \psi_4\ \psi_3'\ \psi_4'$	+	− 0·00655	− 0·000263

NOTATION

$b\,(x_i)_b$ = amount of component i in the bottom product, moles/mole of feed.

$d\,(x_i)_d$ = amount of component i in the top product, moles/mole of feed.

k = order of a determinant.

n = rectifying plates, including the feed plate.

m = stripping plates, including the reboiler.

u_A = product of all terms $(\alpha_A - \phi_p)$, where ϕ_p is any value of ϕ or ϕ' occurring in the alternant being solved.

u_B = similar product of all terms $(\alpha_B - \phi_p)$, etc.

u_1 = product of all terms $(\alpha_i - \phi_1)$, where α_i is the relative volatility of a general component. The product contains a term for each component.

u_2' = product of all terms $(\alpha_i - \phi_2')$, etc.

$(x_i)_f$ = mole fraction of component i in the liquid on the feed plate.

A, B, C, etc., refer to components; in general A being the lightest, B next lightest, etc.

A_1 = abbreviation for $\dfrac{\alpha_A}{\alpha_A - \phi_1}$; $B_1 = \dfrac{\alpha_B}{\alpha_B - \phi_1}$; etc.

A_1' = abbreviation for $\dfrac{\alpha_A}{\alpha_A - \phi_1}$; $B_2' = \dfrac{\alpha_B}{\alpha_B - \phi_2'}$; etc.

V = rectifying section vapour flow, moles/mole of feed.

V' = stripping section vapour flow, moles/mole of feed.

$(X_i)_F$ = mole fraction of component i in the tota feed.

Greek Letters

α_i = relative volatility of component i. All relative volatilities are based on the same component.

ϕ = rectifying section parameter.

ϕ' = stripping section parameter.

ψ_1 = abbreviation for ϕ_1^n, $\psi_2 = \phi_2^n$, etc.

ψ_1' = abbreviation for $1/(\phi_1')^m$, $\psi_2' = 1/(\phi_2')^m$, etc.

ψ_{21} = abbreviation for $\left(\dfrac{\phi_2}{\phi_1}\right)^n$, $\psi_{32} = \left(\dfrac{\phi_3}{\phi_2}\right)^n$, etc.

ψ_{21}' = abbreviation for $\left(\dfrac{\phi_2'}{\phi_1'}\right)^m$, $\psi_{32}' = \left(\dfrac{\phi_3'}{\phi_2'}\right)^m$, etc.

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$\zeta^{\dagger}$ = difference product obtained by subtracting each term in an alternant from each preceding term and multiplying these differences together.

General Subscripts

$o, p, q \ldots r', s', t'$ refer to numeral subscripts on ϕ and ϕ' values.

i refers to a general component.

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The viscosity temperature relationship of liquids

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Summary—A new formula representing the viscosity temperature dependence is proposed. The formula is valid for a variety of liquids, e.g. associated and non-associated liquids, hydrocarbons and mixtures of hydrocarbons. Water, solutions of sucrose in water and of sulphuric acid in water also fit into the system. The same formula can even be applied to mercury. The method can be used for saturated and non-saturated natural mineral-oils, for fatty oils as well as for hydrocarbon mixtures obtained by polymerization and by expelling oxygen from polymerized fatty oils. The proposed formula is generally applicable and more concise and clear than many of the existing equations.

Résumé—Pour représenter la relation température – viscosité, les auteurs proposent une nouvelle formule valable pour une série de liquides : liquides associés et non associés, hydrocarbures, mélanges d'hydrocarbures, eau, solutions de sucre dans l'eau et d'acide sulfurique dans l'eau, mercure, huiles minérales saturées et non saturées, huiles grasses, mélanges d'hydrocarbures obtenus par polymérisation et par réduction d'huiles grasses polymérisées. La formule est générale, plus concise et plus claire que beaucoup d'équations existantes.

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Introduction

It was the intention of the authors to contribute to the study of the connection between viscosity and change of viscosity with temperature respectively and the structure of hydrocarbons and mixtures of hydrocarbons. The first results in this field were obtained with liquid polymers (from definite monomers, olefins of more or less branched character), sometimes containing rings [1, 1a]. Regularities were noticed, particularly in the temperature dependence of the viscosity. Use was made of the de Guzman-Andrade formula [2, 3], in this case applied to mixtures of substances :

$$\log \eta = \frac{A}{T} + B \qquad (1)$$

η = dynamic viscosity in cp.

$\left(1 \text{ cp} = \frac{1}{100} \text{ poise} ; \text{ poise} = \frac{\text{gram}}{\text{cm sec}}\right)$.

T = absolute temperature °K.

A and B = constants.

This formula could be used for classification purposes, but deviations occurred with fractions of higher molecular weight (Fig. 1) beginning with fraction $P\text{-}3_B$, viz. to begin with the fraction having a value of $\eta^{20°C}$ equal to about 1·5 cp.

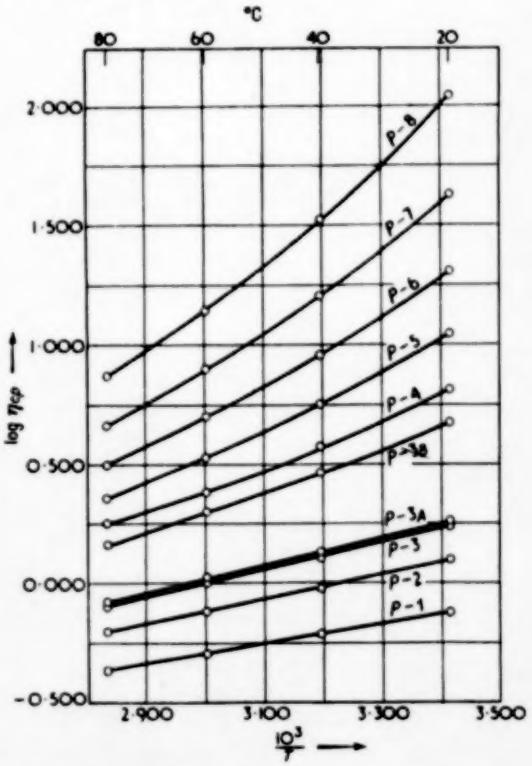

Fig. 1. $\log \eta - \frac{1}{T}$ diagram for polymer-fractions P-1, P-2, etc.

The investigations reached this point before the war and were resumed after the war. New results have been obtained, which have partly been published [4, 5, 6].

It must be remarked that the study of the viscosity temperature relationship is not new: other investigators tried to find formulas connecting viscosity with temperature.

One of the first attempts has been made by POISEUILLE, who gave the formula [7]:

$$\eta = \eta_0 (1 + \alpha t + \beta t^2) \qquad (2)$$

η = dynamic viscosity in cp.
η_0 = dynamic viscosity at $t = 0$°C.
t = temperature °C.
α and β = constants.

Much use is made of the de Guzman-Andrade formula (1); see also [8]. SOUDERS [9] replaced dynamic viscosity by kinematic viscosity and obtained:

$$\log \nu = \frac{A}{T} + B \qquad (3)$$

ν = kinematic viscosity in cs. $\left(1 \text{ cs} = \frac{1}{100}\right.$ stokes; stokes $= \left.\frac{\text{cm}^2}{\text{sec.}}\right)$.
T = absolute temperature °K.
A and B = constants.

Both formulas (1) and (3) fail with associated liquids and with the hydrocarbon mixtures of higher viscosity discussed above, as was already known in the literature for lubricating oils [14].

WALTHER [10] proposed the formula:

$$\log \log (\nu + a) = W - m \log T \qquad (4)$$

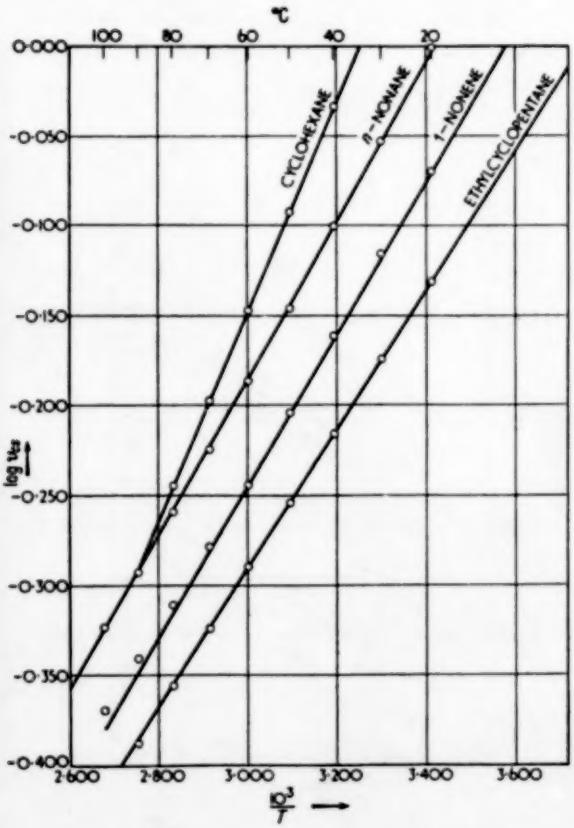

FIG. 2. $\log \nu - \frac{1}{T}$ diagram for a number of hydrocarbons.

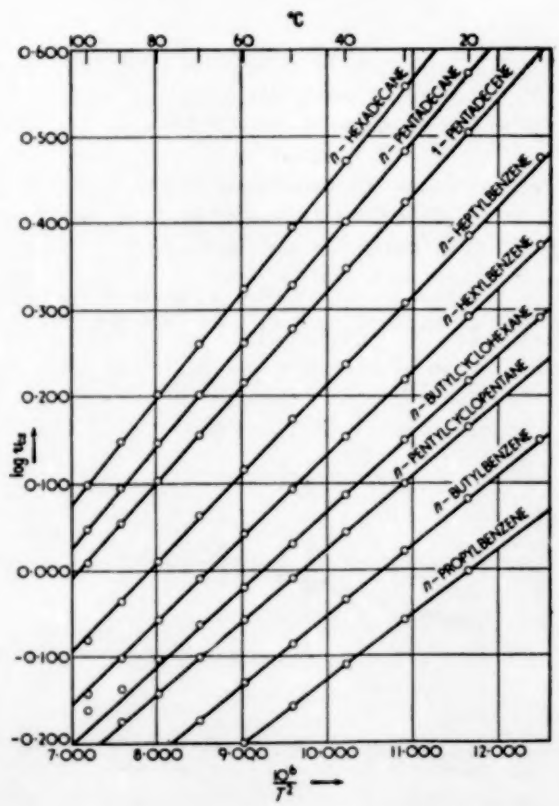

FIG. 3. $\log \nu - \frac{1}{T^2}$ diagram for a number of hydrocarbons.

ν = kinematic viscosity in cs.
T = temperature °K.
a, m, and W = constants.

This formula is often applied to lubricating oils. For general use the difficulty is to determine the value of the constant a. For lubricating oils the value of a is often assumed to be approximately constant, and was considered to have an average value which has been reported successively as 0·8 and 0·6, though a better approximation appears to be 0·7 [10a].

VOGEL [11] proposed the formula :

$$\eta_t = \eta_\infty^{\frac{t-t_1}{t-t_\infty}} \tag{5}$$

η_t = dynamic viscosity in cp at t°C.
η_∞ = dynamic viscosity in cp at $t = \infty$.
t = temperature in °C.
t_1 = temperature at which $\eta_t = 1$.
t_∞ = temperature at which $\eta_t = \infty$.

The formula may be written as :

$$\log \eta = A + \frac{B}{T + C} \tag{6}$$

η = dynamic viscosity in cp.
T = absolute temperature °K.
A, B and C = constants.

In this form the formula is discussed by GUTMANN and SIMMONS [12]; see also [13, 14].

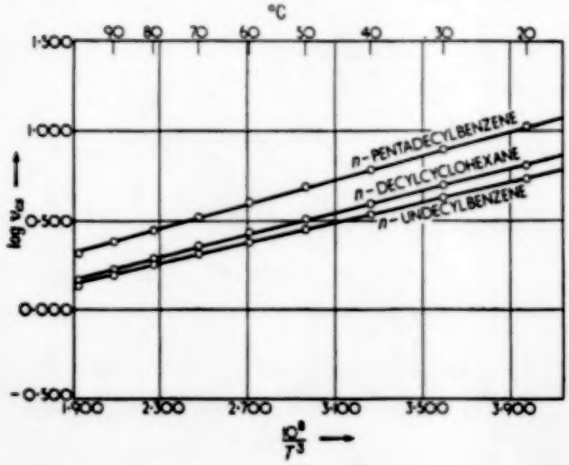

FIG. 4. $\log \nu - \frac{1}{T^3}$ diagram for a number of hydrocarbons.

Recently another formula giving the viscosity temperature dependence was proposed by UMSTÄTTER [15], which may be written as :

$$\text{arc sh ln } \frac{\eta}{A} = B + C \ln T \tag{7}$$

η = dynamic viscosity in cp.
T = absolute temperature °K.
A, B and C = constants.

This formula is discussed by FESSLER [16].

THE NEW FORMULA

It appeared to the authors that the deviations from the de Guzman-Andrade equation (1) or rather the SOUDERS equation (3) were very regular (see Fig. 1).

A new formula, resembling that of SOUDERS, which is hereby proposed, appears to hold in cases in which the SOUDERS equation was not applicable :

$$\log \nu = \frac{A}{T^2} + B \tag{8}$$

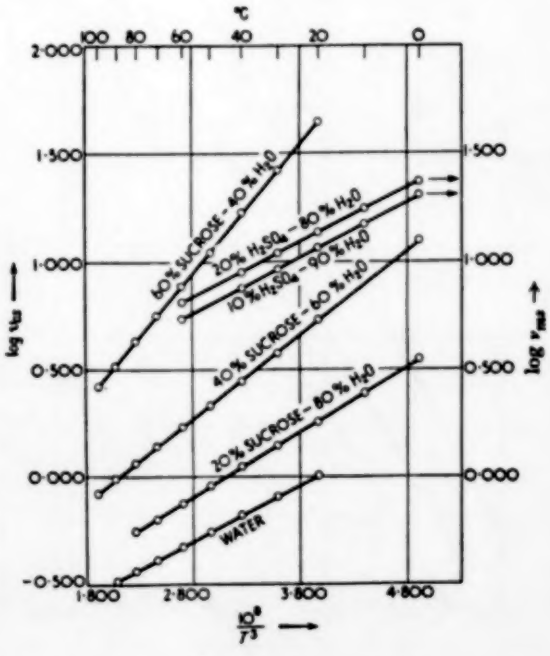

FIG. 5. $\log \nu - \frac{1}{T^3}$ diagram for water, H_2SO_4–H_2O mixtures and sucrose solutions in water.

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ν = kinematic viscosity in cs.
T = absolute temperature °K.
A, B and x = constants.

Graphically this equation is represented by a straight line if log ν is plotted against $\frac{1}{T^x}$ for a particular liquid; B is the value of log ν at $T = \infty$; A gives the temperature dependence of the viscosity of the liquid under examination.

The formula was applied to many liquids; single liquid compounds as well as mixtures of single liquid compounds, non-associated as well as associated liquids.

In order to calculate the value of x in equation (8) for a liquid we have to make three viscosity measurements, ν_1, ν_2 and ν_3 at three temperatures T_1, T_2 and T_3, respectively,

$$\log \nu_1 = \frac{A}{T_1^x} + B$$

$$\log \nu_2 = \frac{A}{T_2^x} + B$$

$$\log \nu_3 = \frac{A}{T_3^x} + B$$

From the former two equations it follows by subtraction that

$$\log \nu_1 - \log \nu_2 = \frac{A}{T_1^x} - \frac{A}{T_2^x} \qquad \text{(a)}$$

and from the latter two:

$$\log \nu_2 - \log \nu_3 = \frac{A}{T_2^x} - \frac{A}{T_3^x} \qquad \text{(b)}$$

(a) and (b) are two equations with the two

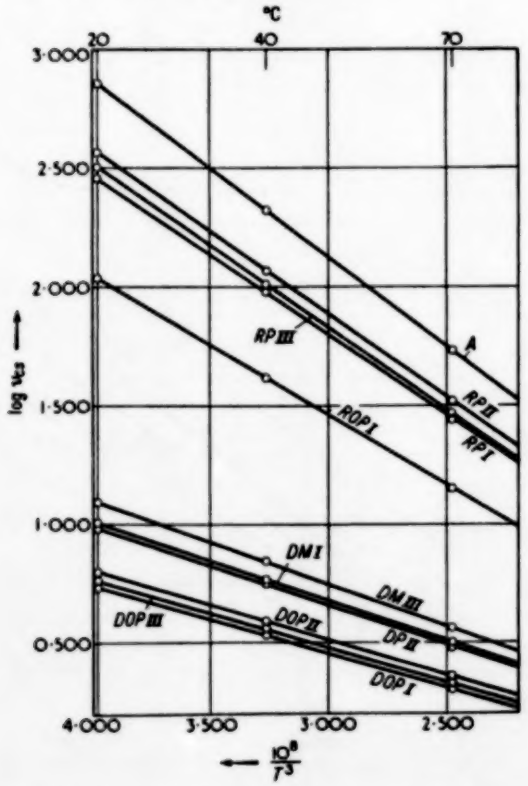

FIG. 6. $\log \nu - \frac{1}{T^3}$ diagram for hydrocarbon mixtures obtained by removing oxygen from polymerized fatty oil fractions.

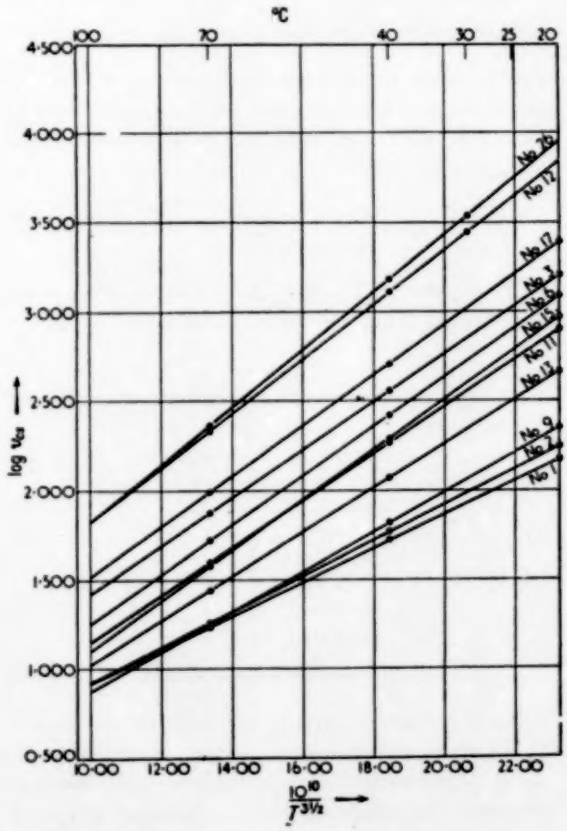

FIG. 7. $\log \nu - \frac{1}{T^{3\frac{1}{2}}}$ diagram for a number of lubricating oils.

unknown constants A and x. By division, the equations can be transformed into :

$$Q = \frac{\log \nu_1 - \log \nu_2}{\log \nu_2 - \log \nu_3} = \frac{\frac{1}{T_1^x} - \frac{1}{T_2^x}}{\frac{1}{T_2^x} - \frac{1}{T_3^x}} \qquad (9)$$

From this equation x may be calculated if ν_1, ν_2, ν_3, T_1, T_2 and T_3 are known. This can be done by calculating the value of Q for various values of x.

As the viscosities were determined at 20°C, 40°C and 70°C ($T_1 = 293$°K, $T_2 = 313$°K and $T_3 = 343$°K), the value of Q may be written as

$$Q \begin{cases} 20 \\ 40. \\ 70 \end{cases}$$

The results are reported in Table 1.

On the other hand if the viscosities ν_1, ν_2 and ν_3 are determined at the temperatures 20°C, 40°C and 70°C, the value of Q may be calculated from equation (9a) :

$$Q = \frac{\log \nu_1 - \log \nu_2}{\log \nu_2 - \log \nu_3} \qquad (9a)$$

By means of Table 1 the value of x may be determined from the calculated value of Q.

Table 1.

$Q \begin{cases} 20 \\ 40 \\ 70 \end{cases}$	x
0·78	1
0·84	2
0·91	3
0·98	4
1·06	5

An important feature of the new formula proves to be that the nearest integral value may be assigned to x without introducing excessive errors in graphical interpolation or extrapolation provided the temperature range is not too large. E.g. the determined value of $x = 2{\cdot}2$; it now proves permissible in equation (8) to use $x = 2{\cdot}0$, instead of $x = 2{\cdot}2$. This gives only a slight deviation from the straight line in the diagram $\log \nu = f\left(\frac{1}{T^{x'}}\right)$ in which x' = nearby whole value of x. It means that only 4 or 5 diagrams (for $x = 1$ to $x = 5$) are necessary for practical use. It also means that for the various members of a group of liquids the values of A, the constant which indicates the temperature dependence of the viscosity, may be compared with each other with the aid of the nearest integral value of x.

EXAMPLES

A large number of viscosity values were determined by means of the Wi. OSTWALD viscometer with improvements worked out by SPROKEL [17]. Other viscosity values were taken from literature

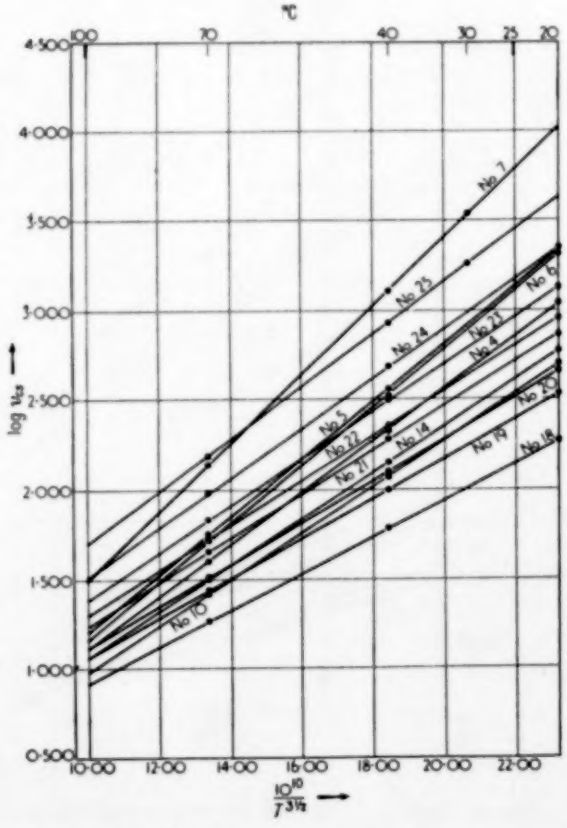

FIG. 8. $\log \nu - \frac{1}{T^{3\frac{1}{2}}}$ diagram for a number of lubricating oils.

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Table 2.

Compound	$\frac{\log \nu_{20} - \log \nu_{40}}{\log \nu_{40} - \log \nu_{70}} = Q$	x	$(\nu_{30})_{pred.}$	$(\nu_{30})_{exp.}$	$\Delta\%$	$(\nu_{40})_{pred.}$	$(\nu_{40})_{exp.}$	$\Delta\%$	$(\nu_{50})_{pred.}$	$(\nu_{50})_{exp.}$
n-Nonane	0·81	1	0·886	0·885	0·1	0·795	0·792	0·4	0·719	0·716
		2	0·895	0·885	1·1	0·794	0·792	0·3	0·712	0·716
n-Pentadecane	0·86	2	3·05	3·03	0·7	2·523	2·518	0·2	2·132	2·128
n-Hexadecane	0·86	2	—	—	—	2·954	2·962	− 0·3	2·473	2·479
Et-Cyclopentane	0·79	1	0·670	0·669	0·1	0·609	0·608	0·2	0·558	0·557
n-Pentylcyclopentane	0·85	2	1·263	1·254	0·7	1·103	1·102	0·1	0·978	0·978
Cyclohexane	0·81	1	—	—	—	0·924	0·926	− 0·2	0·808	0·808
n-Butylcyclohexane	0·87	2	1·409	1·406	0·2	1·222	1·217	0·4	1·074	1·069
n-Tridecylcyclohexane	0·88	3	8·18	8·11	0·9	6·27	6·26	0·2	4·92	4·99
n-Decylcyclohexane	0·89	3	5·01	4·98	0·6	3·97	3·96	0·3	3·21	3·24
n-Nonene-1	0·78	1	0·762	0·766	− 0·5	0·688	0·690	− 0·3	0·624	0·625
n-Pentadecene	0·83	2	2·64	2·65	−0·4	2·21	2·22	−0·5	1·89	1·89
n-Propylbenzene	0·83	2	0·8741	0·8745	0·0	0·7759	0·7770	− 0·1	0·6972	0·6979
n-Butylbenzene	0·82	2	1·048	1·049	− 0·1	0·923	0·925	− 0·2	0·822	0·818
n-Hexylbenzene	0·86	2	1·661	1·650	0·8	1·426	1·419	0·5	1·240	1·239
n-Heptylbenzene	0·87	2	2·04	2·03	0·5	1·722	1·722	0·0	1·483	1·488
n-Undecylbenzene	0·88	3	4·28	4·23	1·2	3·45	3·43	0·6	2·84	2·85
n-Pentadecylbenzene	0·89	3	7·80	7·92	− 1·5	6·05	6·15	− 1·6	4·83	4·92

Compound	$\Delta\%$	$(\nu_{70})_{pred.}$	$(\nu_{70})_{exp.}$	$\Delta\%$	$(\nu_{80})_{pred.}$	$(\nu_{80})_{exp.}$	$\Delta\%$	$(\nu_{90})_{pred.}$	$(\nu_{90})_{exp.}$	$\Delta\%$
n-Nonane	0·4	0·599	0·597	0·3	0·552	0·550	0·4	0·510	0·510	0·0
	− 0·6	0·590	0·597	− 1·2	0·542	0·550	− 1·5	0·504	0·510	− 1·2
n-Pentadecane	0·2	1·587	1·590	− 0·2	1·393	1·400	− 0·5	1·239	1·244	− 0·4
n-Hexadecane	− 0·2	1·819	1·822	− 0·2	1·583	1·593	− 0·6	1·402	1·408	− 0·4
Et-Cyclopentane	0·2	0·475	0·474	0·2	0·442	0·44	0·5	0·413	0·41	0·7
n-Pentylcyclopentane	0·0	0·792	0·792	0·0	0·722	0·72	0·3	0·664	0·67	− 0·9
Cyclohexane	0·0	0·635	0·634	0·2	0·569	0·569	0·0	—	—	—
n-Butylcyclohexane	0·5	0·858	0·863	− 0·6	0·776	0·79	− 1·4	0·711	0·73	− 2·6
n-Tridecylcyclohexane	− 1·4	3·33	3·37	− 1·3	2·81	2·80	0·4	2·41	2·36	2·1
n-Decylcyclohexane	− 0·9	2·27	2·30	− 1·3	1·95	1·96	− 0·5	1·71	1·69	1·2
n-Nonene-1	− 0·2	0·524	0·527	− 0·6	0·484	0·489	1·0	0·449	0·456	− 1·5
n-Pentadecene	0·0	1·43	1·43	0·0	1·267	1·269	− 0·2	1·135	1·132	0·3
n-Propylbenzene	− 0·1	—	—	—	—	—	—	—	—	—
n-Butylbenzene	0·5	0·674	0·671	0·4	—	—	—	—	—	—
n-Hexylbenzene	0·1	0·977	0·980	− 0·3	0·876	0·876	0·0	0·796	0·792	0·5
n-Heptylbenzene	− 0·4	1·149	1·157	− 0·7	1·024	1·025	− 0·1	0·925	0·920	0·5
n-Undecylbenzene	− 0·4	2·06	2·07	− 0·5	1·80	1·779	1·1	1·59	1·555	2·3
n-Pentadecylbenzene	− 1·8	3·33	3·36	− 0·9	2·83	2·81	0·7	2·46	2·40	2·5

In this table ν is given in centistokes.

data. For each liquid the value of x was calculated by means of equation (9a) and Table 1.

In the first place the results of interpolation of viscosities at various temperatures of some hydrocarbons [18] will be shown. The values of $Q\left(Q\begin{Bmatrix}20\\40\\70\end{Bmatrix}\right)$ and x are calculated from the viscosities at 20°C, 40°C and 70°C. The viscosities at 20°C, 60°C and 100°C were used to construct the straight line in the diagram $\log \nu = f\left(\frac{1}{T^x}\right)$. The viscosities at 30°C, 40°C, 50°C, 70°C, 80°C and 90°C were predicted and compared with the experimental values from literature, see Table 2 and the corresponding diagrams, Figs. 2, 3 and 4.

Table 2 shows that the nearest whole value of x may be taken without making large errors in the interpolation. E.g. the value of x of n-nonane is 1·5 (Table 1). Either the diagram $\log \nu = \mathrm{f}\left(\frac{1}{T}\right)$ or the diagram $\log \nu = f\left(\frac{1}{T^2}\right)$ may be used.

The consequent deviation rarely exceeds 1·5%, which is about equal to the experimental error. The nearest whole value of x may be taken only if the temperature range is not too large, e.g. from 20°C to 100°C. If the range covers several hundreds of degrees Centigrade a more exact value of x has to be chosen (see below).

Further examples are given in Table 3. See also Fig. 5.

In Table 3 predicted values (obtained by graphical interpolation) and experimental values are given of a sucrose solution in water (containing 60% sucrose by weight), a H_2SO_4–H_2O mixture (containing 20% H_2SO_4 by weight) and water itself.

The value of $Q\left(Q\begin{Bmatrix}20\\40\\60\end{Bmatrix}\right)$ of the H_2SO_4–H_2O mixture is calculated from viscosities at 20°C, 40°C and 60°C. The corresponding value of x can be read from Table 4.

As can be seen from Table 3 good agreement exists between predicted and experimental values of viscosity.

In Fig. 5 data for water, two H_2SO_4–H_2O mixtures and three sucrose solutions in water are

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Table 3.

Temp. °C.	60% sucrose–40% H_2O			20% H_2SO_4–80% H_2O			*Water*		
	$(\nu_{cs})_{pred.}$	$(\nu_{cs})_{exp.}$	Δ%	$(\nu_{ms})_{pred.}$	$(\nu_{ms})_{exp.}$	Δ%	$(\nu_{cs})_{exp.}$	$(\nu_{cs})_{pred.}$	Δ%
0				23·7	23·5	0·9			
10				17·58	17·55	0·2			
20	44·0	43·9	0·2	13·65	13·56	0·7	1·007	1·004	− 0·3
30	26·2	26·35	− 0·6	10·93	10·80	1·2	0·804	0·805	0·1
40	16·63	16·66	− 0·2	8·95	8·94	0·1	0·661	0·661	0·0
50	11·04	11·01	0·3	—	—	—	0·556	0·552	− 0·7
60	7·78	7·76	0·3	6·48	6·48	0·0	0·477	0·472	− 1·0
70	5·66	5·66	0·0				0·415	0·414	− 0·2
80	4·29	4·29	0·0				0·367	0·363	− 1·1
90	3·34	3·314	0·8				0·328	0·326	− 0·6
100	2·685	2·678	0·3				0·296	0·296	0·0
Q	$Q\begin{Bmatrix}20\\40 = 0{\cdot}90\\70\end{Bmatrix}$			$Q\begin{Bmatrix}20\\40 = 1{\cdot}30\\60\end{Bmatrix}$			$Q\begin{Bmatrix}20\\40 = 0{\cdot}91\\70\end{Bmatrix}$		
x	3			3			3		

Table 4.

Q { 20 40 60	x
1·14	1
1·21	2
1·29	3
1·37	4
1·46	5

plotted in a $\log \nu - \frac{1}{T^3}$ diagram, T ranging from 273°K–373°K (0°C-100°C).

In Fig. 6 data for mixtures of hydrocarbons obtained by removing oxygen from polymerized fatty oil fractions [19] are plotted in a $\log \nu - \frac{1}{T^3}$ diagram. Measurements were made at 20°C, 40°C and 70°C. The value of x for all these fractions appeared to be about 3. The viscosity values ranged from 5 cs to 700 cs. The hydrocarbon mixtures contained from about 0 to 3 rings per molecule.

Next data of 25 lubricating oils are plotted in two $\log \nu - \frac{1}{T^{3\frac{1}{2}}}$ diagrams (Fig. 7 and Fig. 8). Measurements were made at 20°C, 40°C and 70°C.

The values of Q { 20 40 70 for these lubricating oils ranged from 0·91 to 0·99 and consequently the values of x from 3 to 4 (see Table 1). The average value of $x = 3\frac{1}{2}$ was chosen to construct the $\log \nu - \frac{1}{T^{3\frac{1}{2}}}$ diagram.

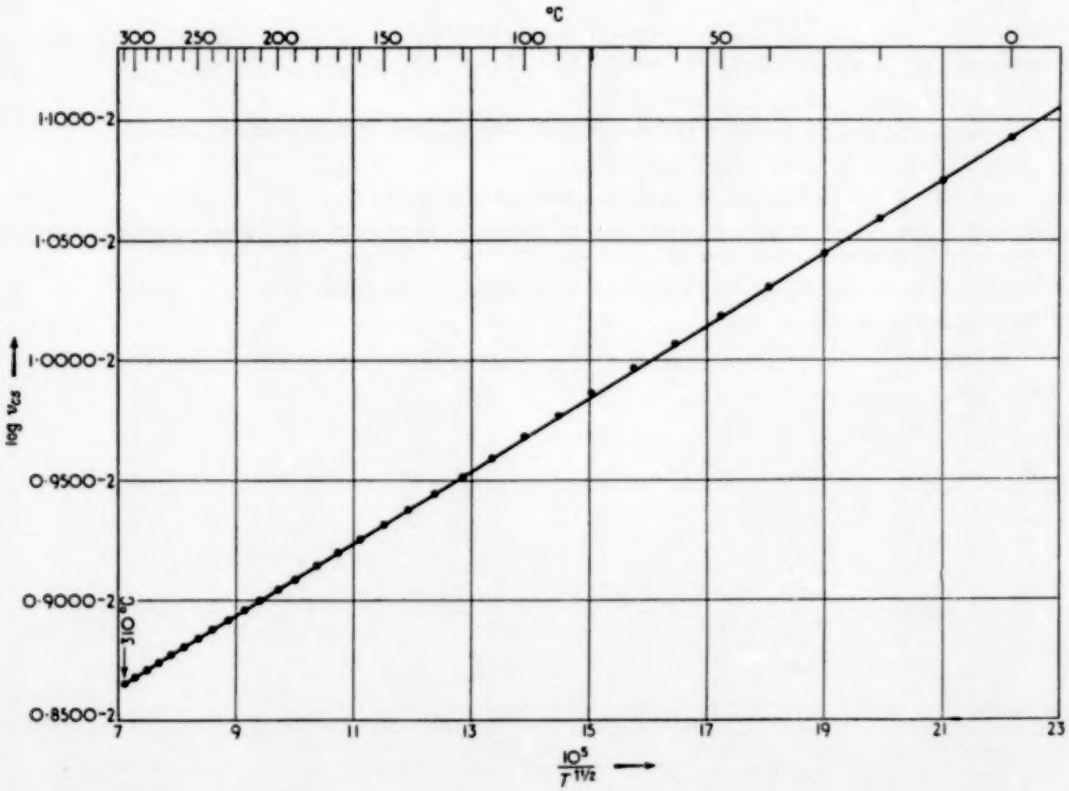

FIG. 9. $\log \nu - \frac{1}{T^{1\frac{1}{2}}}$ diagram for mercury.

Finally data of viscosity values of mercury [20] are shown in Fig. 9. The value of x appeared to be $x = 1\frac{1}{2}$. The temperature ranges from 0°C to 310°C. As may be seen from the diagram $\log \nu = f\left(\frac{1}{T^{1\frac{1}{2}}}\right)$ mercury also satisfies equation (8).

The authors intend to develop their research work in various directions.

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Book reviews

Chemical Engineering in Practice. Edited by JAMES I. HARPER. Reinhold Publishing Corporation. 24s.

IN May, 1953, a meeting was held by the American Institute of Chemical Engineers at the University of Pennsylvania at which eight authors read papers concerned with the putting of a chemical process into successful commercial operation. These papers have been edited by J. I. HARPER and are collected in this small volume to put before the young chemical engineer some of the problems that may beset him and the way they can be solved.

The first three chapters are on Process, Research and Development engineering and are illustrated by the laboratory investigations in the production of high octane gasoline from catalytic reforming of petroleum naphthas; the design and construction of pilot plants, and the selection of the most economic design illustrated by the production of hydrogen, either by hydrolysis or by propane reforming.

The next chapter is on Economic Analysis and shows how the annual return on investment or the payout period (i.e. the number of years that will elapse before the invested cash is recovered) can be estimated. There are then three chapters on Project, Construction and Operational Engineering corresponding to the problems encountered in detailed design, in construction on the site in operating the plant to bring it into production.

The final chapter is on "Market Research Engineering" although it is difficult to see how the term engineering can be included. It is illustrated by those amateurish pseudo-comic sketches beloved by the Americans, but which only raise a puzzled expression on the faces of their foreign colleagues. Market research has so many imponderables that it would be a rash manufacturer who entrusted this work to junior and unexperienced staff to whom these lectures are addressed.

It would have been more instructive if the eight authors could have collaborated to show these stages of development with a single process as was attempted in "A Problem in Chemical Engineering Design" issued by the Institution of Chemical Engineers for the more limited field of process and project engineering. The price is very high compared with other books now available in the chemical engineering field.

M. B. DONALD

WARREN K. LEWIS, ARTHUR H. RADASCH, H. CLAY LEWIS: **Industrial Stoichiometry.** McGraw-Hill Book Co. Inc. 35s.

THE sub-title of this book is "Chemical Calculations of Manufacturing Processes." It was first published in 1926. The dictionary definition of stoichiometry is "the branch of chemistry treating of chemical combination in definite proportions." To those who took the chemical engineering practice school at M.I.T. it was the method by which the efficiency and method of operation of any chemical process could be studied without the necessity of the paraphenalia of weighing machines, flow meters, tapping holes in reaction vessels, the means by which the process could be analysed with the least possible interference with its normal operation. It is to be hoped that one day mechanical engineers will realize its usefulness in assessing boiler performance and drop the calculations of weight of air required for combustion when they invariably order their fans on volume.

The change in the second edition is indicated by the increase in size from 174 to 429 pages. The chapter on Fuels and Combustion is split into Gaseous and Liquid Fuels on the one hand and Solid Fuels on the other. The chapter on Gas Producers is now headed Secondary Fuels. There are additional chapters on Energy Balances and Equilibrium, Nitrogen Compounds, Fixed Alkalis and Ceramics. Crystallization and furnace design chapters disappear. The chapter on Equilibrium contains a comprehensive graph of the equilibrium constants for combustion reactions against temperature; Nitrogen Compounds include ammonia and nitric acid, Fixed Alkalis deals with the manufacture of soda ash and its causticisation; Ceramics treats the use of binary phase rule systems and that of magnesia-aluminia-silica for the solution of problems.

If the book is not already the standard text book of all schools of chemical engineering it certainly should be, as indeed it can almost now be included under the category of a classic in the subject.

M. B. DONALD

W. MATZ (Farbwerke Hoechst): **Anwendung des Aehnlichkeitsgrundsatzes in der Verfahrenstechnik.** Springer-Verlag, Berlin, 1954. 115 pages. DM 13.50.

THE main purpose of this book, as stated in the preface, is to introduce the reader to the principle of similitude and to the theory of models, as well as to show the possibilities of practical application. After an introductory chapter entitled "General Remarks" the author in the second chapter deals with the "Theory of Similitude." It is a difficult task to explain in an exact, logical and at the same time clear and simple form this theory and the theory of dimensions, far more difficult than it is to apply the results of these theories to practical problems. Dr. MATZ does not intend to contribute to the theoretical aspects. It is a pity, therefore, that in trying to be complete, he develops the theory from three different starting points, viz. from the

proportionality factors of the physical constants, from the differential equations governing the phenomena and from the physical dimensions of the quantities under study. For the reader who studies this subject for the first time this multitude of derivations may be embarrassing. Besides, the treatments are not quite exact. E.g., the foundation of the theory of similitude on differential equations remains rather vague. It does not become clear from the treatment that the differential equations of two similar systems become identical if both the coefficients and the boundary conditions are made dimensionless. The author has not made use of the opportunity to elucidate in this section the definition and the implications of the principle of similitude of two systems from a mathematical point of view.

The third and most extensive chapter of the book is devoted to engineering applications. In the examples the author gives rather a large part of the normal non-dimensional theory of the unit operations involved and from this the reader is led to the rules for similarity and the use of dimensionless numbers. In a book that is intended to explain the methods of dimensional analysis it would have been more logical to stress the fact that these methods can be used without solving the problem analytically.

In some of the examples, where the author shows that exact similarity is not possible, an explanation is given of very useful artificial corrections which can be applied to the model in order to reach a satisfactory degree of similarity.

Some details of the treatment may be criticized. The reviewer cannot agree, for instance, with the treatment of the power consumption of a paddle stirrer on page 57, where the power number is given as a function of the Froude number only. Moreover, the power number as plotted on the ordinate of Fig. 12 is not dimensionless. It is the reviewer's personal feeling that some other introductions to the subject which appeared in the English language (e.g. the excellent book of L. LANGHAAR, *Dimensional Analysis and the Theory of Models*) are to be preferred, but for those to whom these English texts are not accessible this book provides a sufficient basis for the application of the very useful principles of similitude.

Th. N. ZWIETERING

H. FISCHER: Elektrolytische Abscheidung und Elektrokrystallisation von Metallen, 717 pp. 247 illustrations. Springer, Berlin. DM. 72.00

IN HIS preface to the book Professor FISCHER states that it was his purpose to write a fundamental (grundlegendes) work covering the whole range of scientific principles connected with the study of the electro-deposition of metals. In so doing he hoped to establish a scientific foundation for the relatively new subject of "electro-crystallisation."

The first part (some 320 pages), of the book is devoted to the fundamentals of electrochemistry with particular reference to cathodic processes. It includes a section of over one hundred pages dealing with the role of inhibitors.

Part two deals with "electro-crystallisation." After introductory sections on the kinetics of crystal growth in general and on the mechanism of electrolytic crystallisation in particular, the author goes on to discuss the structure of electrodeposits, presenting his material in terms of the system originated by him some five years ago. There is a short final section dealing with non-metallic inclusions.

Part three discusses the theoretical aspects of the most important properties of electrodeposits, including brightness, internal stress and hardness. The forty-two pages of part four list values of some of the above properties for the deposits of many of the important metals. The final five pages are devoted to alloy deposits.

The reader of this book will find that in it is collected a large range of material which has hitherto been dispersed throughout the literature. The book is well indexed and it will therefore prove valuable as a source book, although the text itself is not designed for easy reference.

It is unfortunate that a tendency to over-elaboration makes the book difficult to read. All the data relating to the structure of polycrystalline electrodeposits are arranged in terms of the previously mentioned system of the author's. One wonders whether this part of the book would not have been more useful as a source of information, had the facts been presented independently of the system and the latter described in a separate section; it would have benefited by more thorough illustration and the microphotographs could perhaps have been selected from a wider field. One would, for example, have expected to see one of the classical photographs of ERDEY-GRUZ and VOLMER of silver or copper deposits on single crystal spheres. Many readers will be a little worried by explanations in terms of, for example, "strengthened, but still moderate, inhibition."

These criticisms having been made it is necessary to state that Professor FISCHER has rendered an invaluable service by undertaking such a laborious task of compilation. There is little doubt that the book will prove valuable to anyone concerned with the fundamentals of electrodeposition.

H. J. PICK

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